THE

TECHNICAL ANALYSIS OF BRASS

AND THE

NON–FERROUS ALLOYS

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BRASS ANALYSIS

PART I — INTRODUCTION

CHAPTER I

ENGINEERING ALLOYS

In a paper read before the American Society for Testing Materials, in 1903, Mr. G. H. Clamer, second vice-president and chemist of the Ajax Metal Company, stated that there were at that time in service of the railroads of the country on 1,600,000 cars 160,000,000 pounds and on 39,900 locomotives 5,000,000 pounds of bearing metal. At an average price of 13 cents per pound this represented a money value of $21,450,000. Add this to the bearing metal on engines, rolling mills, shafting and machinery of all sorts and the amount would have been easily doubled. In view of the increase in the amount of machinery and rolling stock it is safe to say that the value of the bearing metal now in use is considerably over fifty million dollars. Alloys are also extensively used for machinery and parts for which the metals steel and iron, ordinarily used for such purposes, cannot be employed because of the ease with which they rust and corrode or because a lighter or showier metal is desired.

Some alloys are also not corroded by sea water, while others are not attacked by acids or alkalies, and hence are suitable for the manufacture of propellers of steamships, acid pumps, etc.   Again, alloys are often harder or stronger than the soft metals, such as copper for example, and may be employed to advantage where the electrical conductivity properties of copper are desired coupled with greater strength than the metal alone would have, etc. Alloys melt at a lower temperature than do the component metals and hence may be employed for solders, fusible plugs, etc.   In view of the many engineering uses of alloys, their study is one which is well worth the time of the chemical engineer.

BEARING METALS

Bearings are usually composed of alloys of copper, lead, tin, antimony and zinc, and are known as Babbitt metal, white metal, brass, phosphor bronze, etc., and by various trade names.   Some of the alloys are patented (as for example the "plastic bronze" in Table I), but most of them are merely sold under a trade name, and as they are often made of scrap, are, in some instances, of uncertain composition even for the same brand.

The principal qualities which a good bearing metal should have are, first, good antifriction properties so as to withstand heavy loads at high speeds without heating, and second, sufficient compressive strength neither to be squeezed out of place under a high pressure nor to crack or break when subjected to sudden shocks.

Theoretically all metals have the same friction (Thurston) and the value of the soft white alloys for bearings lies mainly in their ready reduction to a smooth surface after any local impairing of the surface, such as would result from the introduction of any foreign matter between the moving surface and the bearing. In this latter case the soft alloys flow or squeeze from the pressure into the irregularity, forming a larger area for the distribution of the pressure; and the larger the area over which the pressure is extended the less liability is there to overheating, etc.

Lead flows more easily than any of the common metals, and hence it has the greatest antifrictional properties.

Lead is also the cheapest of the metals except iron, the relative values and prices, May 1, 1908, being:

	CENTS PER LB.
Lead	4
Zinc	$4\frac{3}{4}$
Antimony	$8\frac{3}{4}$
Copper	13
Tin	32

Lead of itself, however, is too soft to be used alone, as it cannot be retained in the recesses of the bearing. If antimony is added to the lead it increases its hardness and brittleness, and if tin is also added it makes a tougher alloy than lead and antimony alone. Most of the Babbitt metals now on the market are alloys of lead, tin and antimony. In such babbitts the wear increases with the antimony, and the price with the tin.

The high-antimony babbitts are most used in heavy machinery, as they are harder, while those low in antimony are used in the more rapidly run machinery. The soft babbitts do not usually have enough strength to sustain the weight and shocks of heavy machinery bearings and so are generally used as a liner, which is run into a shell of brass, bronze or gun metal.

In Table I will be found some examples of Babbitt metal. The original inventor is said to have used a mixture of 12 parts tin, 2 parts antimony and 1 part copper. This would be a very expensive babbitt, however. The wide divergence in the composition of babbitt is shown by the table. Babbitt A is said to be a good alloy for high-speed machinery, as its antifrictional properties are great, but it is not very hard. It melts at about 500° F. (260° C.). Babbitt B is somewhat harder. It melts at 491° F. (255° C.), and has been used for many years by a well-known firm for lining the heavy bearings on marine engines. Babbitt D is still harder and is suitable for very heavy machinery. Babbitts C, E and G are recommended by Davis ("Friction and Lubrication") as being very successful. Babbitt F is an example of a high zinc bearing alloy, recommended by C. R. Tomkins (*Mechanical News*, January, 1901) as having great wearing properties and also great resistance properties. This alloy, however, does not possess very great antifriction properties and so cannot be used where speeds higher than 300 R.P.M. are employed. The white metal, white

brass, " Magnolia metal " and car brass lining may also be looked upon as babbitts. The white brass has about four times the electrical conductivity of ordinary babbitt, and hence is recommended for use in the bearings of generators, motors, electric cars, etc. Tempered lead is harder than pure lead and is supposed to have great antifrictional value for the following reason: In use, the sodium hydroxide formed by the oxidation of the sodium in the alloy is supposed to form a soap with the oil and so assist lubrication. In order for this reaction to take place, however, the oil must contain animal matter, since mineral oils do not saponify.

TABLE I. — BEARING METALS

Alloys.	Analysis.						
	Lead.	Tin.	Anti-mony.	Copper.	Zinc.	Iron.	Other con-stituents.
Babbitt A.........	80.0	20.0	.....	.....	.....	.....	
Babbitt B.........	72.0	21.0	7.0	.....	.....	.....	
Babbitt C.........	70.0	10.0	20.0	.....	.....	.....	
Babbitt D.........	80.5	11.5	7.5	0.5	.....	.....	
Babbitt E.........	0.5	68.0	.....	1.0	31.5	.....	
Babbitt F.........	.....	20.0	.....	.....	80.0	.....	
Babbitt G.........	.....	86.0	10.0	4.0	.....	.....	
White metal.......	82.0	.....	12.0	6.0	.....	.....	
White brass........	.....	64.0	.....	2.00	34.0	.....	
"Magnolia metal"	80.0	4.75	15.0	trace	.....	.....	Bi = 0.25
Car brass lining....	80.5	11.5	7.5	0.5	.....	.....	
"Ajax plastic bronze".........	30.0	5.0	.....	65.0	.....	.....	
"Ajax metal".....	11.5	11.5	.....	77.0	.....	.....	
P. R.R. car brass B.	15.0	8.0	.....	77.0	.....	.....	
"S bearing metal"	9.5	10.0	.....	79.7	.....	.....	P = 0.80
"Delta metal"....	5.1	2.4	.....	92.4	.....	0.1	
"Carmelia metal "	14.8	4.3	.....	70.2	10.2	0.5	
Tempered lead.....	98.5	0.08	0.11	.....	.....	.....	Na = 1.30

Alloys of copper, tin and lead also make excellent bearing metals when lined with a thin skin of lead or babbitt. They wear much better than the soft babbitts. Examples of such alloys are shown in Table I. In such alloys it has been proved by experiment that the tendency to wear decreases with increase of lead and the decrease of tin. Increase of lead also increases the antifrictional value of the alloy and hence its tendency to become heated. In these alloys a certain amount of tin is necessary to keep the lead from separating from the alloy. By using a little nickel in the mixture and care in its making and pouring, the Ajax Metal Company have succeeded in making an alloy containing 30 per cent lead, called "Ajax plastic bronze." In this alloy no segregation takes place and the bearings as they wear are continually in contact with the soft antifriction particles of lead, which are in turn backed up by the harder particles of copper. In brasses, structure has much to do with the antifriction properties, as a bearing in which segregation takes place, causing hard spots, is more or less likely to cause friction. It is therefore the practice to add small amounts of phosphorus or arsenic or one or two per cent of zinc to keep the mixture homogeneous. A good bearing metal should have as fine a grain as possible in connection with the greatest toughness and hardness. To examine the grain, an occasional brass should be broken, say one in each one hundred.

Of the alloys given in the table, the " S phosphor bronze " was for a long time used by the

Pennsylvania Railroad Company, who discontinued its use in favor of the " P. R. R. brass B." The " Ajax metal " and the " Ajax plastic bronze " are both made by the Ajax Metal Company and are extensively used for car brasses. " Carmelia metal " and " Delta metal " are also used as bearing metals.

Phosphor tin is an alloy of tin and phosphorus, containing about 5 per cent tin. It is extensively used in making phosphor bronze, the patents on which have now expired.

Solders and Fusible Alloys

Practically all of the solders are alloys of lead and tin. The more lead the alloy contains above 40 per cent the higher will be its melting point and also the less it contains below 40 per cent the higher will be its melting point. If bismuth is added to these alloys, the melting points are lowered. Alloys of bismuth, lead and tin are of very low melting points, and addition of cadmium still further lowers the melting point of such alloys.

Table II shows the composition of some solders and fusible metals. The solders E, F, G and H are those ordinarily used by plumbers and tinsmiths. Solder F is the one most generally used, while H is especially adapted to use with lead and tin pipes. Solder I has a very low melting point and is intended for household mending, as it can be dropped on a leak from an old spoon and melted over a gas jet or candle. Hard solders contain more or less copper. A good white hard solder

TABLE II. — SOLDERS AND FUSIBLE METALS

Alloy.	Composition.					Melting Point.	
	Lead	Tin.	Bismuth.	Cadmium.	Other constituents.	°C.	°F.
Solder A.............	96.15	3.85	.....	.....	....	292	558
Solder B.............	90.9	9.1	.....	.....	....	283	541
Solder C.............	83.3	16.7	.....	.....	....	266	511
Solder D...........	75.0	25.0	.....	.....	....	250	482
Solder E.............	66.7	33.3	.....	.....	....	227	441
Solder F.............	50.0	50.0	.....	.....	....	188	370
Solder G.............	40.0	60.0	.....	.....	....	168	334
Solder H...........	33.3	66.7	.....	.....	....	171	340
Solder I.............	33.3	33.3	33.3	.....	....	140	284
Steam boiler plug alloy A.............	48.4	.....	12.8	.....	Zn=38.8	171	340
Steam boiler plug alloy B.............	44.5	.....	22.2	.....	Zn=33.3	141	285
Steam boiler plug alloy C.............	42.1	.....	42.1	.....	Zn=15.8	123	253
Steam boiler plug alloy D...........	10.0	40.0	50.0	.....	....	116	240
Sir Isaac Newton's alloy.............	30.0	20.0	50.0	.....	....	100	212
Alloy suitable for casts.............	31.25	18.75	50.0	.....	....	98	208
Rose's alloy........	28.1	21.9	50.0	.....	....	95	203
D'Arcet's alloy.....	25.0	25.0	50.0	.....	....	93	200
Wood's alloy.......	25.0	12.5	50.0	12.5	....	60	140
Lipowitz's alloy.....	26.9	12.7	50.0	10.4	....	66	150
Expanding alloy.....	66.7	.....	8.3	.....	Sb=25.0	66	150

contained copper, 60 per cent; tin, 20 per cent; zinc, 20 per cent; and a fairly easily melted yellow hard solder, analyzed copper, 43.75 per cent; zinc, 56.25 per cent. Most aluminum solders are alloys of tin and aluminum, containing from 15 to 25 per cent aluminum. Novel's aluminum solder consists of tin alloyed with from 1 to 1½ per cent copper or nickel.

The fusible alloys are used in engineering work

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for fusible plugs in boilers, fusible plugs in electrical wiring, for delicate castings and for filling up defective places in ornamental castings. For fusible plugs in boilers the United States Government uses pure Banca tin. If a lower melting point alloy is desired, one of the fusible alloys in Table II may be used. Fusible alloys are used in electric circuits as current interrupters. Serving as conductors on short lengths of circuit, they melt as soon as the current becomes too strong. Rose's alloy, D'Arcet's alloy and Wood's alloy may all be used for this purpose. If a melting temperature between that of the last two alloys is needed, substituting cadmium for 5 to 10 per cent of tin in D'Arcet's alloy will lower the melting point according to the cadmium added.

Bismuth possesses the unusual quality of expanding on cooling. It is, therefore, introduced in many alloys to prevent or reduce shrinkage in the mold. For this reason the bismuth alloys are excellent for making delicate castings. The more fusible of these alloys, Wood's and D'Arcet's, can be used for making soap molds and for taking impressions from paper or wood molds. For filling out defective places in castings, the expanding alloy given in the table is used. Sometimes defects in structural steel have been hidden by its use, followed by a coat of paint — a dishonest practice on which it is well to be posted. Type metal, pewter, stereotype metal, Britannia metal, etc. (see table IV), are all fusible alloys of industrial rather than engineering importance.

The melting point of alloys which fuse at a low temperature may be found by tying a small wire around a fragment of the alloy and suspending in a bath of water, if under 212° F., or melted paraffine, if above this temperature. A thermometer is kept in the bath and the temperature of the latter gradually raised until the alloy melts. The temperature of the bath is then noted as the melting point of the alloy.

Foundry and Rolling-mill Alloys.

Of the engineering alloys used in making parts of machinery the alloys of copper, zinc and tin play the most important part. The alloys of copper and zinc are known as brass and those of copper and tin as bronze. Additions of other metals and of phosphorus, arsenic, silicon, etc., give to both brass and bronze special properties and fit them for special uses. The composition and properties of these alloys are given below.

Brass. — To insure good castings copper-zinc alloys should always contain at least 15 per cent zinc. Between 17 and 30 per cent zinc, brasses all show practically similar properties. They have about the same strength (30,000 pounds) and ductility. From 30 to 41 per cent zinc, brass increases in tensile strength with the content of zinc and decreases in ductility. Its tensile, transverse and torsional strength reach its maximum at 41 per cent zinc. All brass containing less than 55 per cent zinc is yellow; after that point it turns white, and as the zinc increases the metal becomes

weaker and more brittle.   For wire and sheet brass
an alloy containing about 33 per cent zinc is best, as
at this composition it possesses the greatest ductility.
Brass for sheets, rods and wire should contain
practically no antimony.   Tin is often added to
brass to harden the alloy, and lead makes it machine
easily; too much lead, however, makes it brittle.
The more copper brass contains the better its
electrical conductivity.   In Table III will be found
some examples of the composition of brass used
for various purposes.

Brass A is intended for use where good clean sand
castings are desired.   It has a good yellow color,
will run free and cut clean.   If a stronger alloy is
desired, increase the tin slightly.   Brass B is recom-
mended by Sperry for trolley fittings, clips, holders,
cars, etc.   Less tin makes it too soft, more tin lowers
the conductivity.   Lead makes the fittings easily
machined, but too much would make them brittle.

Brass C is suitable for sheets.   Brass for such
purposes should be low in lead and tin and contain
practically no antimony (less than 0.02).   The
figures given for tin and lead are also safe limits
to stay under.   Brass containing as much as 38
per cent zinc still has a high ductility and is tougher
than that given.   If a redder brass is desired one
containing from 70 to 80 per cent copper and 30 to 20
per cent zinc may be used.

Bronze is supposed to be an alloy of tin and copper,
but commercial bronze nearly always contains zinc,
which is added to improve and cheapen the alloy.
Alloys of copper and tin reach a maximum tensile

strength at about 4 per cent tin. They get harder
as the tin increases, until finally they become too
brittle to cut with a tool. Alloys of copper and
tin only are rarely used and nearly all bronzes
contain more zinc than tin. Alloys of copper and
tin alone, however, resist acids and alkalies much
better than do those containing zinc, and where
castings are exposed to such corrosive liquids a
strictly copper-tin alloy will give the best results.
Silicon, phosphorus, iron and manganese, when
added in small amounts, add to the strength of
bronze. Zinc is added to bronze as a deoxidizer.
It also makes a cheaper alloy. In Table III will
be found the composition of various bronzes.

Bronze A is that of the U. S. Navy, and C is
the Admiralty metal of the British navy, used for
parts of marine engines. Bronze E is the old
" gun-metal " used for cannon, etc. Bronze B is
used for whistles of shrill tone; if a lower-toned
whistle is desired the tin is reduced to about 17 per
cent. Bronze D is used for large bells; for smaller
bells the tin is increased until for hand bells, etc.,
the tin may reach $33\frac{1}{3}$ per cent. Bronze F is
suitable for art tablets, etc., and bronze G for
statuary, etc. In this latter class of work it is
necessary that the bronze become thinly fluid on
fusing, fill the molds out sharply, be easily worked
with a file and take on the green coating (called
patina) after short exposure to the air. Genuine
bronze does not fill out the molds well and it is
difficult to obtain homogeneous castings from it.
A bronze containing from 4 to 5 per cent tin and

from 10 to 20 per cent zinc is, therefore, generally used for statues. Bronze of the composition given F has an orange-red color. If a lighter color is desired more zinc is used.

TABLE III. — FOUNDRY AND ROLLING-MILL ALLOYS

Alloy.	Composition.						Used for.
	Copper.	Zinc.	Tin.	Lead.	Iron.	Other constituents.	
Brass A	67.1	28.7	2.4	1.8			Brass castings.
Brass B	87.0	6.0	4.0	3.0			Trolley fittings.
Brass C	67.0	32.0	0.5	0.5			Wire and sheets.
Bronze A	88.0	2.0	10.0				U. S. navy.
Bronze B	80.0		18.0			Sb=2.0	Steam whistles.
Bronze C	87.0	5.0	8.0				British navy.
Bronze D	80.0		20.0				Bells.
Bronze E (gun metal)	90.0		10.0				U. S. ordnance (1875).
Bronze F	88.8	2.8	5.6	2.8			Tablets.
Bronze G	85.0	10.0	5.0				Statuary.
Phosphor bronze	90.0		9.8			P=0.20	Stronger than bronze.
Silicon bronze	97.12	1.14	1.10			Si=0.05	Telegraph wire.
Delta metal	55.94	41.61		0.72	0.87	{Mn=0.81, P=0.013}	
Aich's metal	60.0	38.2			1.8		
Tobin bronze	61.20	37.44	0.90	0.36	0.18		
Muntz metal	57.55	40.02	1.40	0.56	0.38		
Retz alloy	74.3		11.4	8.9		Sb=5.4	Acid receivers.
Manganese bronze	57.20	40.14	1.18	0.02	1.33	{Mn=0.02, Al=0.1}	Propeller blades.
Hydr. metal	83.05	6.00	10.81	0.10			Mine pumps.
Acid-resisting metal	82.05	2.00	8.00	8.00		P=0.05	
Alkali-resisting metal					95.0	Ni=5.0	
Phono electric metal	98.55		1.40			Si=0.05	Telephone wires.
Manganin	83					{Mn=13, Ni=4}	Resistance.
Trolley wheel bronze	92.0	2.0		6.0			Trolley wheels.

Phosphor Bronze has been mentioned among the bearing alloys. Phosphorus is added to bronze as a deoxidizer, hence but a small percentage is required. Zinc should never be present in phosphor bronze, as it causes liquation of the tin and consequently "tin spots." Phosphor bronze is usually made from copper, tin and phosphor tin. The

latter alloy usually contains 5 per cent phosphorus and is sometimes adulterated with lead. About one or two pounds of phosphor tin per 100 pounds of alloy are usually enough. Phosphor bronze of the composition given, cast from remelted ingots, will have a tensile strength of from 40,000 to 50,000 pounds per square inch. It is used principally in cases where great strength and power as well as resistance to corrosion are required. It can be rolled, hammered and stretched. For rolling purposes it should not contain more than 0.05 per cent phosphorus and very little lead. It should also not contain more than 5 per cent tin for ordinary purposes, although it can be rolled with as high as 8 per cent tin when desire for great strength necessitates it. For casting purposes, phosphor bronze may contain 10 per cent tin and 0.5 per cent phosphorus. For very strong castings no lead should be present.

Aluminum Bronze. — This alloy contains from $1\frac{1}{4}$ to 11 per cent aluminum and the remainder copper. It varies from a tensile strength of 25,000 pounds for $1\frac{1}{4}$ per cent aluminum to 90,000 pounds for the 11 per cent aluminum alloy. More than 11 per cent aluminum produces a brittle alloy. Aluminum bronze shrinks more than ordinary brass in casting, and hence care is required in pouring, etc., into the molds. Aluminum bronze containing less than $7\frac{1}{2}$ per cent aluminum can be rolled, swedged, spun or drawn cold, and it can all be worked at a bright-red heat.

Manganese Bronze. — Pure metallic manganese

exerts a very marked bleaching action upon copper, $18\frac{1}{2}$ per cent manganese in the copper alloy being sufficient for a white color. Twenty to 30 per cent manganese may be added to copper without impairing its ductility, although doubling its strength. Alloys of copper and manganese oxidize badly, and alloys of manganese, zinc and copper produce a casting full of blowholes. If $1\frac{1}{4}$ per cent aluminum is added to a manganese-copper alloy it serves as a deoxidizer and the alloy may be cast readily, producing perfect castings. Manganese bronze, as ordinarily understood, however, contains very little manganese, usually less than 1 per cent. It has a tensile strength of approximately 60,000 pounds when cast and 70,000 pounds when rolled, and is used principally for casting propeller blades, as it is not corroded by sea water.

Silicon Bronze is bronze in which silicon instead of phosphorus has been used. It is more ductile and elastic than phosphor bronze, does not rust and is very strong. It is used principally for telegraph and telephone wires.

Iron-Brasses (Delta metal, Aich's metal, Muntz metal, Tobin bronze, etc.). — These are all brasses or bronzes in which iron has been used to harden the alloy. A very small percentage of iron serves the purpose. These alloys are very strong and tough and tarnish very little.

Non-corroding Alloys. — Retz alloy resists the corrosion of acids and can be used in the manufacture of receivers for which porcelain and ebonite are usually required.

Hydraulic Metal offers special resistance to corrosion by acid mine waters, and hence is used for mine pumps, etc.   It has a tensile strength of about 30,000 pounds.

Acid-resisting Metal. — This alloy will resist the action of nitric acid and is used successfully for sulphide pulp mill machinery.   It is quite strong.

Gun Metal is also used for the pumps employed to keep a supply of dilute acid running down the towers of the Mond gas-producing system, as this metal is scarcely at all attacked by this acid.   The use of manganese bronze in sea water has been noted.

Alkali-resisting Metal. — This may contain as much as 10 per cent nickel and is used in soap works, etc., where caustic alkalies are employed.   Alloys containing zinc, tin, lead, aluminum and antimony are quickly corroded by caustic alkalies.

Special Electrical Alloys. — Phono-electric alloy is used in place of pure copper when a strong wire is required, as it has a much higher tensile strength than the latter metal.   It has, however, only about 40 per cent of its conductivity.

Manganin is used as a resistance material.   The nickel increases its melting point, permitting a higher heat without danger of fusion, and also decreases the temperature coefficient of electrical resistance.

Trolley-wheel bronze is used for trolley wheels. The lead increases the wearing qualities and the zinc gives solidity to the casting.   Silicon bronze

and brass for trolley fixtures have been already mentioned.

Light Alloys. — These all contain aluminum for a base. An alloy of aluminum with 5 per cent copper and nickel combined was used for rolling the plates of the racing yacht *Defender*. It had a tensile strength of 40,000 pounds, and a specific gravity of 2.75. An alloy of aluminum with 15 to 25 per cent zinc and some copper is also used to some extent for casting spur gears, parts of machinery, etc. It has a tensile strength of 22,000 to 45,000 pounds and a density of 3 to 3.4, according to the percentage of zinc. These alloys are rigid and wear well. When they contain less than 15 per cent zinc they can be rolled, but above that are brittle. Casting in chills increases the tensile strength of aluminum-zinc alloys. Professor J. W. Richards considers the magnesium-aluminum alloys the best all around of the light aluminum alloys. They contain from 2 to 10 per cent magnesium, and the latter, when water-chilled, shows a tensile strength of 61,100 pounds and an elongation of 4.2 per cent.

Table III gives the composition of some foundry and rolling-mill alloys.

Besides the alloys of engineering importance, many alloys are used for the manufacture of scientific apparatus, household utensils, hardware, printing type, trimmings for wood and leather work, etc. Samples of these occasionally find their way to the chemist for analysis, hence Table IV is inserted here and gives the composition of the more important of these alloys.

TABLE IV. — MISCELLANEOUS ALLOYS

Alloy.	Composition.							Uses.
	Lead	Tin	Anti-mony.	Cop-per.	Zinc.	Iron.	Other con-stituents.	
Mosaic gold.....				65.0	35.0		....	Imitation gold.
Pinchbeck.......				83.3	16.7		....	Imitation gold.
Mannheim gold..				80.0	20.0		....	Imitation gold.
Dutch gold......				84.5	15.5		....	Imitation gold leaf; very ductile.
Britannia metal .		90.1	6.3	3.1	0 5		....	Household utensile and ornaments.
Improved Britannia metal...		90.1	7.44	2.31			Mn=0.15	Manganese gives finer grain than Britannia metal
Kayserzinn......		92.98	5.44	1.58			....	Britannia metal under German name.
Pewter..........		20.0	80.0				....	Household utensile and ornaments.
Ashberry metal .		79.0	15.0	3.0	2.0		Ni=1.0	Household utensils and ornaments.
Minorfer........		66.0	20.0	4.0	9.0	1.0	....	Household utensils and ornaments.
Bath metal......				55.0	45.0		....	Household utensils; harder than Britannia metal.
German silver...				61.8	19.1		Ni=19.1	Imitation silver instruments and scientific apparatus.
Stellite.........							{Cr=75.00 {Co=25.00	Cutlery; non-corrosive; hardness equal to mild steel.
Argentan........				52.0	22.0		Ni=26.0	Imitation silver.
Victor metal....				49.94	34.27	0.28	{Ni=15.40 {Al=0.10	Whiter than above two; not attacked by sea water.
Hardware metal				50.00	34.90		{Ni=15.0 {Al=0.10	Harness trimmings; only used for sand castings.
Minargent.......				56.8			{ Ni=39.8 { W=2.8 { Al=0.6	Imitation silver.
Sterline				68.50	12.84		Ni=17.88	Imitation silver.
Needle metal....	1.77	7.96		84.96	5.31		....	Can be cast in fine forms.
Japanese bronze .	9.9	4.7		82.7	1.8		....	Japanese art bronze.
Speculum metal.		29.11		70.24	trace		{Fe, Ni { traces	Reflectors, etc.
Stereotype metal	20.0	30.0					Bi=50.0	Stereotyping.
Type metal......	70.0	10.0	18.0	2.0		0.76	....	Type.

CHAPTER II

APPARATUS FOR ELECTROCHEMICAL ANALYSIS

MANY metals can be more conveniently determined electrolytically than by any other method, and means for carrying out such determinations should be provided in every well-equipped metallurgical laboratory, no matter how small it may be. In determining copper, nickel, bismuth, etc., the electrolytic methods are far more satisfactory than the precipitation or volumetric ones, hence in a laboratory where bearing metals or alloys are analyzed means should be provided for electrolytic work.

Use of the Electric Lighting Current. — Stillwell and Austin[1] were, we believe, the first to suggest the use of the electric lighting current for the determination of metals in the electrolytic way, and the writers have found this to be not only sufficient for ordinary technical purposes but also by far the most convenient. When available, it is much cheaper than batteries and saves the operator much trouble. The only disadvantage in connection with its use is the constant voltage, which is usually 110 or 220. Indirect or alternating currents must of course be transformed to direct currents. This necessitates the use of a trans-

[1] Jour. Anal. and App. Chem., VI, 129.

former, which may make the cost of installation of
the outfit for electrolytic work so great as to make
the use of batteries preferable to that of the electric
lighting current.

It is of course necessary to reduce the strength
of the current. For this purpose the resistance
board shown in Fig. 1 and designed by one of the
authors is convenient and satisfactory. It consists
of a stout board 2 inches thick and 24 inches by
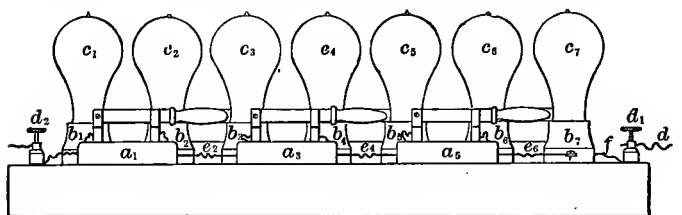8 inches. This board should have its top covered

Fig. 1.

with a piece of asbestos board, to guard against
fire, etc., so that the apparatus may be left over-
night without danger. In a line down the middle
of this board, with their centers three inches apart,
seven porcelain keyless sockets or receptacles, b_1,
b_2, b_3, etc., should be fastened. The best form of
receptacle to use is that shown in the cut. Single-
pole knife switches, a_1, a_2, a_3, etc., are also placed
three on each side, as shown in Fig. 2. At either
end of the board a binding post d_1 and d_2 is placed.
Each receptacle is connected to the next receptacle
and also to one point of the switch, by means of
short pieces of insulated copper wire. The end

receptacles are also connected each to a binding post. All the connections should be made as shown.

With this board should also be provided six 16-candle-power lamps, six 32-candle-power lamps, six 50-candle-power lamps, and a safety plug of say 10 amperes. To use the board, connect one of the binding posts to one terminal of the electric light current and connect the other with one of the electrodes of the solution to be electrolyzed. Now, if a weak current is desired, screw 16-candle-power
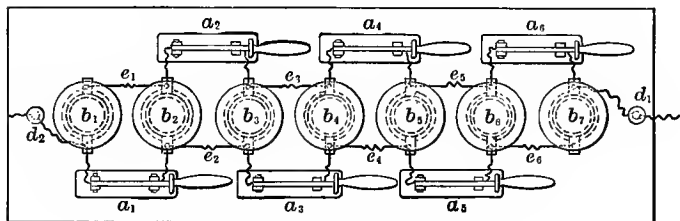

Fig. 2.

lamps into the sockets and open all the switches. The current will then travel through all seven of the lamps, as follows: from d_2 through the lamp c_1, and from this to the lamp c_2, by means of the wire e_1, and thence to the binding post d_1 through e_2, c_3, e_3, c_4, e_4, c_5, e_5, c_6, e_6, c_7, in order. For a resistance of six lamps, remove the lamp c_7, and place the safety plug in the receptacle b_7. For five lamps, close the switch a_6; for four lamps, the switch a_5; for three lamps, a_4; for two lamps, a_3, and for one lamp, a_2.

For stronger currents the lamps may be put in parallel. To do this, take out the safety plug

from b_7, close all the switches and put in from one
to seven lamps, according to the strength of current
desired. Seven lamps will give about 3.5 amperes,
while two lamps will give about one ampere. For
yet stronger currents put in the 32-candle-power
or the 50-candle-power lamps. For very weak
currents, use another board and shunt the current
through this around a light. For analytical work,
however, the above board is sufficient and only
16-candle-power lamps need be used, unless the
rotating anode is to be employed, when 50-candle-
power lamps will be needed, since the currents for
this work are much stronger.

The above board provided with 16-candle-power
and 50-candle-power lamps will give a range of
current of from about 0.07 ampere to about 11.0
amperes. The resistance of the board can be calcu-
lated sufficiently near the truth for analytical pur-
poses, by assuming for a 110-volt circuit that the 16-
candle-power lamps have a resistance of 220 ohms,
the 32-candle-power lamps, 108 ohms and the 50-
candle-power lamps 69 ohms. If, therefore, seven
16-candle-power lamps are in series, according to
Ohm's law

$$\text{Amperes} = \frac{\text{volts}}{\text{ohms}} \quad \text{or} \quad \text{Amperes} = \frac{110}{220 \times 7} = \frac{1}{14},$$

or the resistance of the lamps is $\frac{1}{14}$ ampere or
0.07 ampere. If now the seven 16-candle-power
lamps are in parallel the resistance will be $\frac{110}{220} \times 7$,
or 3.5 amperes.

Instead of calculating the resistance of the board,

it is preferable to determine it by means of an ammeter as described below.

To start with a low resistance and increase to a greater, place all seven lamps in the board and open all the switches and connect up the apparatus with the terminal wires. Now take out the lamp c_7 and screw the safety plug in the receptacle b_7. Then close in turn the switches a_6, a_5, a_4, a_3, and a_2. Do not close the switch a_1, however, or short-circuiting will take place. Now take out the plug from the receptacle b_7 and unscrew all the lamps, except c_1, from the receptacles, far enough to break the contact. Close the switch a_1 and screw in the lamps to make contact one by one.

To avoid short-circuiting, the connection between b_1 and d_2 or between b_7 and d_1 should be made with fuse wire, or another lamp receptacle may be put in between the receptacle b_7 and the binding post d_1, connected to b_7 and d_1 by pieces of wire, and a safety plug kept in this socket all the time.

The board may be fastened to the wall or, where space is limited, a cord and plug socket may be fastened to it so that it can be put away in a desk when not in use. When wanted the board can be readily attached to the current by screwing the plug socket into a lamp receptacle on the wall or hanging from the ceiling.

Gravity Cells. — When the electric lighting current is not at hand, batteries must of course be used. For ordinary analytical work six crowfoot or gravity cells will be found sufficient and these

can be arranged in series or in parallel as the case
may require. No resistance board is needed, as
the strength of the current can be controlled by the
number and the arrangement of the cells them-
selves. Where currents of greater strength than
one or two amperes are needed the bichromate cell
should be used in place of the gravity cells. When
weak currents are to be used, however, nothing
will be found so easy to take care of as the crowfoot
or gravity cells. These may be arranged in a
closet under the work table on which the electrolytic
work is done. They should be connected up to a
board as shown in Fig. 3, so that they can be
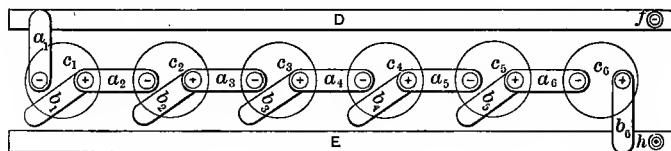readily arranged in any way desired.

Fig. 3.

This board consists of two narrow strips of copper
or brass, E and D, running along the front edge or
on the side of the work bench just under the top.
These strips should have a binding post at either
end of which the wires leading to the anode and
cathode of the solution to be electrolyzed should
be connected, and should be about six inches apart.
Equidistant between the two strips of metal twelve
short pieces of brass spring, a_1, b_1, a_2, b_2, etc., should
be screwed into the board. These springs should
be about $3\frac{1}{2}$ inches long and should reach to either

the strip D or E. Each pair of springs should be placed so that the adjacent spring of the following pair can rest on the screw holding the spring itself to the board. That is, referring to Fig. 3, the spring a_2 should be so placed that it can be swung around so as to rest on either the copper strip E or D or on the screw holding the spring b_1 to the board. Each spring should be connected to a pole of a battery. The springs a_1, a_2, a_3, etc., should be connected to the zincs of the cells, and the springs b_1, b_2, b_3, etc., should be connected to the coppers of the cells. Fig. 4 shows an elevation of one of
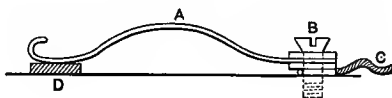

Fig. 4.

the springs. A is a piece of brass spring with a round hole bored in one end and the other turned up to form a handle. This spring is fastened to the table by means of the brass screw B, and should be held in place by two washers, as shown. C is a piece of copper wire connecting the spring with the battery. D is the long copper strip running the length of the table.

With the springs in the position shown in Fig. 3 the six cells are in series. The spring a_1 connected with the zinc of cell c_1 rests on the strip D, and the spring b_6 connected with the copper element of cell c_6 rests on the strip E, while the copper elements of the cells c_1, c_2, c_3, c_4 and c_5 connected to the zinc elements of the next cell by means of the

A description of storage batteries, their use and care, is beyond the range and scope of this book; an excellent chapter on storage batteries, written by Prof. F. B. Crocker, will, however, be found in a little book, " Practical Lessons in Electricity," published by The American School of Correspondence at Armour Institute of Technology, Chicago, Ill., which any one interested in the subject of electrochemistry will do well to procure.

Rheostat. — Where batteries or storage cells are used some means other than the lamp board previously described must be provided, since the resistance of this is far too great for such source of current.   Rheostats are manufactured for this purpose, made up with coils of resistance wire and a movable arm that can be placed so as to allow the current to pass through as much of the resistance as desired.   Such rheostats are best purchased. They should be constructed so that they will cut down the current from one cell, from full strength to about 0.105 ampere, in from ten to twenty equal steps; and be able to withstand the full current from all the batteries at once.

A water rheostat makes a very cheap and simple means of controlling the current.   A glass or earthenware jar of about three quarts' capacity is filled with a very weak solution of sulphuric acid. Two arc lamp carbons are attached to the terminals of the current in series and dip into the solution. The farther the carbons are apart the greater the resistance.   By fastening one on the edge of the jar and hanging the other on the edge with a clip

springs a_2, a_3, a_4, a_5 and a_6 should rest on the strip D and those marked b_1, b_2, b_3, b_4, b_5 and b_6 should rest on the strip E.

A battery of six crowfoot cells can be bought for less than $5.00.

Storage Batteries. — Storage batteries are a very convenient source of current when means for charging them is at hand, and a board like that described above will be found very handy for connecting them up. Their relatively high voltage and amperage make them more suitable than any other forms of battery, while their discharge is very steady and dependable. They give a voltage of about 2. A higher voltage is obtained by adding more cells in series (i.e., the positive pole of one to the negative pole of the next, and so on).

Cells can be obtained for any amperage capacity, the amperage required to exhaust the cell in eight hours being the standard. A cell of two and a half amperes for eight hours' discharge is large enough for ordinary use, although it is convenient to have cells of a larger capacity so as to allow longer intervals between charges.

Unfortunately, storage batteries cannot be used unless there is some means at hand for charging them, and moreover they are very delicate and need careful attention to prevent them from being ruined. Explicit directions accompany the batteries, and if means for charging them, such as the lighting circuit and a rheostat sufficient to reduce the current to the normal charging rate, are at hand, nothing better for electrolysis can be obtained.

so that it may be placed anywhere, an excellent
rheostat is obtained. The resistance in the solu-
tion can be decreased by adding acid, and increased
by adding water. The sizes of the jar, etc., will
depend upon the conditions of the circuit, and are
easily found by experiment.

Arrangement of Cells. — The diagrams (Figs. 5
and 6) show how certain results can be obtained by
altering the àrrangements of the connections. It
must be noted that a voltage above the desired
figure must be obtained by adding batteries in
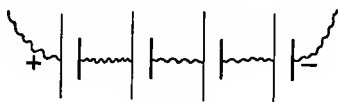series and then cutting down to the right point by

Fig. 5.

the rheostat. As mentioned before, by the series
arrangement the cells add their voltage to the cir-
cuit, but the amperage remains about the same as
for one cell. Fig. 5 represents the series arrange-
ment, in which the short thick lines represent the
zincs and the long thin lines the coppers. The
irregular lines represent connecting wires. If $3\frac{1}{3}$
volts are desired, the voltage is brought up to four
by adding four cells and then reducing the voltage
to $3\frac{1}{2}$ by the rheostat. This arrangement will give
an amperage depending upon the resistance in the
circuit and electrolyte. It should in most cases be
sufficient, since the current usually required is very
small, but if it is not, the amperage can be doubled
by adding an equal number of cells in parallel.

Fig. 6 represents this arrangement. This is a series-parallel arrangement, giving the same voltage as in Fig. 5 but twice the amperage. It will be noticed that there are four groups of cells. In each group there are two cells with the zinc connected to zinc and the copper to copper. But the zincs of one group are connected to the coppers of the next, and so on. In making these arrangements, the
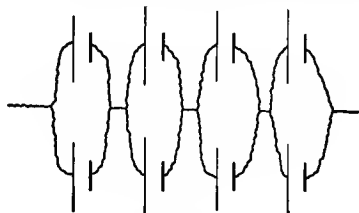

Fig. 6.

same proportions always hold true, so that any combination of cells, to give almost any current, can be obtained.

Electrodes. — In electrochemical analysis, a platinum wire or spiral is usually used as an anode, Fig. 7, and a platinum dish, cone or cylinder for the cathode. When the deposit to be weighed is formed on the anode the cone or dish is used as the anode and the spiral for the cathode. Aluminum cathodes have been proposed for copper analysis, and even copper ones would probably give satisfactory results in this case. When obtainable, however, platinum should be used.

Fig. 7.

The most satisfactory cathode is a small platinum dish weighing about 30 to 50 grams. When large

volumes of solutions have to be electrolyzed the
cone or cylinder must, of course, be used and the
solution held in a beaker.

Some determinations can best be carried out with
the mercury cathode. This in its simplest form
consists of a small narrow beaker of about 50 cc.
capacity, near the bottom of which there is intro-
duced through the side a thin piece of platinum
wire. The portion of this wire inside the beaker
dips into the mercury, which usually should just
cover the bottom of the beaker, while the external
portion curves around under the beaker so that
when the latter rests upon a piece of copper plate,
which is in turn attached to the negative pole of a
source of current, connection is made and the mer-
cury becomes the cathode. The mercury is washed
first with water, then alcohol and finally ether.

Among the numerous devices for shortening the
time required for electrochemical determination
the gauze electrodes deserve mention. These usu-
ally consist of small cylinders of platinum gauze
which have been well roughened by means of a
sand blast. A convenient form and size is a corru-
gated cylinder about one inch in diameter and one
and one-half inches long, made from fifty-two-mesh
wire gauze. With this form of electrode deter-
minations can be made nearly as quickly as by the
use of the rotating anode or the Frary solenoid.

Stands. — Fig. 8 shows a convenient stand
for use when a platinum dish is employed as a
cathode. It consists of a wooden block, *A*, about
2 inches thick and 4 or 5 inches square, depending

on the size of the dish. A round hole about an inch deep and about 3 inches in diameter should be gouged out of this and a triangle, C, of copper wire fastened above this, as shown in the illustration, by two round-headed screws, f_1 and f_2, and a binding post, e. A light wooden frame, B, should be fastened to the block, A, and the binding post, d, screwed midway in the top piece of this. The binding post d should be for two wires, and the second hole should be directly over the center of the triangle. The dish to be used as a cathode should rest on the wire triangle, and the platinum wire to be used for an anode should pass through one hole of the binding post d. The wires carry-

Fig. 8.

ing the current can then be attached one $(+)$ at the vacant hole of the binding post d and the other $(-)$ at the binding post e. When a cone or a cylinder is used as a cathode the block A should be made solid, without the hole, and the frame should be high enough to permit a beaker to be
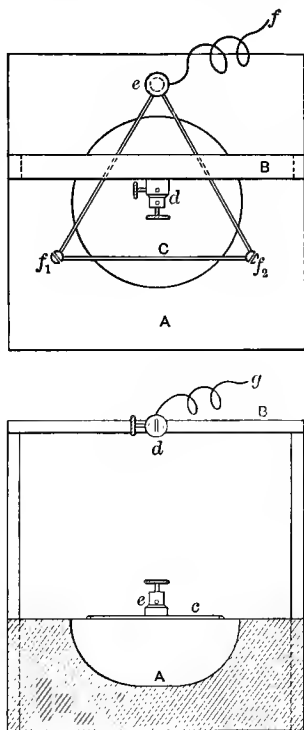
moved in and out under it comfortably. Another
binding post similar to *d* should then be fastened
beside *d* to hold the cone.

Very often supports similar to retort stands,
except that the supporting rod must be of heavy
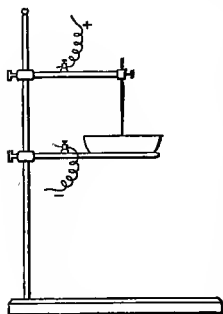glass to avoid short circuits, are used. Fig. 9
shows such a stand. The sup-
porting arms or rings can be
obtained with binding posts to
receive the terminals, and must
be of bright metal, not painted.
If the platinum dish is used it
sets directly upon a ring clamped
to the glass supporting rod. It
is preferable to provide this ring
with three platinum points for
contact with the dish. If the
dish is to be heated, a sheet of
asbestos is fastened on the underside of the ring in
order that heat may be applied to the solution with-
out the dish coming in contact with the bare flame.

Fig. 9.

Measuring Instruments. — For measuring the
current there will be needed an ammeter and a
voltmeter.

The ammeter, Fig. 10, measures the amperage
or amount of current. The instrument should
read from $\frac{1}{100}$ of an ampere to at least 2 amperes.
It is connected with the circuit in series, as in
Fig. 6.

The voltmeter, Fig. 11, registers the volts or force
of the current. It should read from $\frac{1}{4}$ to 10 volts.
It is placed, as mentioned before, in parallel, and

between the precipitating vessel and all other parts of the circuit.

Where the current is to be measured, the proper method of assembling the circuit is shown in Fig. 12.
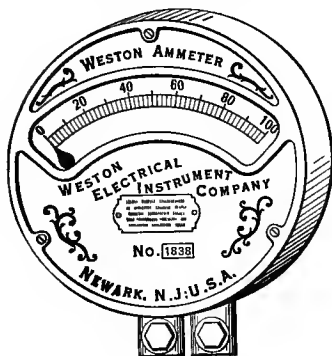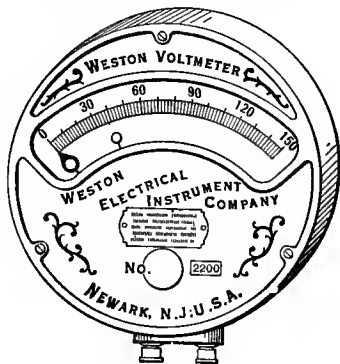

Fig. 10.   Fig. 11.

It will be noted that the rheostat and ammeter are in series and the voltmeter in parallel.   There must be no other instrument between the voltmeter and
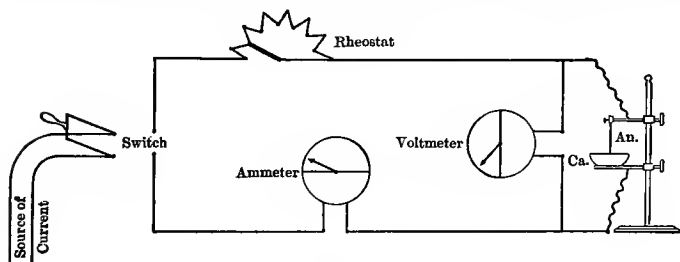
Fig. 12.

the precipitating dish, as the true voltage between the anode and the cathode will be given by this position only.

Rotating Anode. — Many electrochemical determinations can have the time necessary for complete deposition of the metal greatly shortened by rotating the anode. Means for doing this are described below. For the cathode a platinum dish is best suited.

The anode used is a spiral about two inches in diameter, made of heavy platinum wire. It is made slightly bowl-shaped so that it will remain immersed in the liquid in spite of the funnel-shaped form assumed by the latter on rotating the anode. Fig. 13 shows its construction.
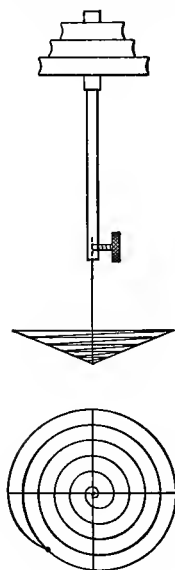
Any suitable means for revolving the anode may be used providing the rotations per minute are high enough. A water motor, electric motor, or even power derived from shafting will answer. But undoubtedly an electric motor run by the lighting circuit is the most convenient. The anode is driven by a small round belt, and the use of cone or stepped pulleys will be found convenient, as several speeds can be gotten in this way. Fig. 14 shows the general arrangement.

Fig. 13.

The anode should revolve at about 700 revolutions per minute.

When many determinations have to be made at the same time, one motor may of course be made

to do for all by crossing the belt after each pulley. In this case the motor and bearings of the anodes should all be mounted on the same framework.
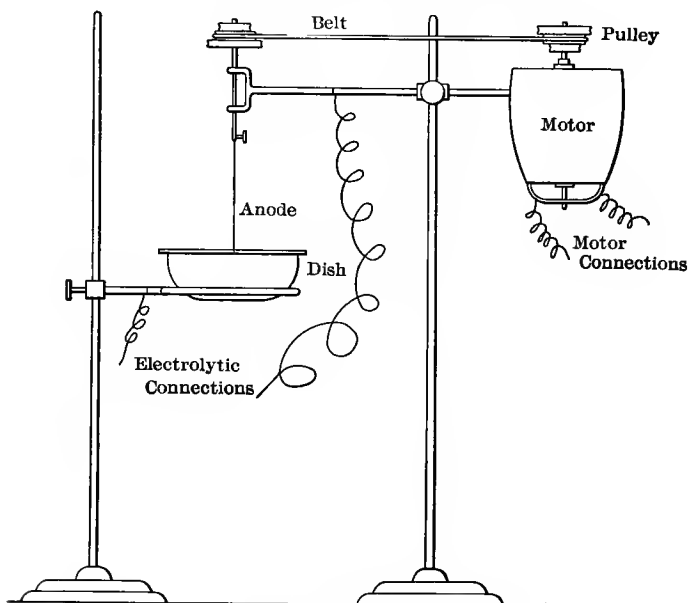
Fig. 14.

The Frary Solenoid. — This consists of about 500 turns of 1.5 mm. insulated copper wire (No. 14 B. & S. gauge) wound about a copper cylinder 6 cm. in diameter and 11 cm. high (see Fig. 15). The flanges at the end of the cylinder are of sheet iron. A hollow cylinder, 4 cm. high and made of iron 1 cm. thick, stands in the lower part of the copper cylinder, and the solenoid is surrounded by a sheet-iron mantle 2 mm. thick., The cathode may be

of platinum foil, but should be preferably of gauze, and should be large enough to fit the beaker quite closely. This latter should hold from 125 to 150 cc. The anode may be spiral, of platinum wire. The
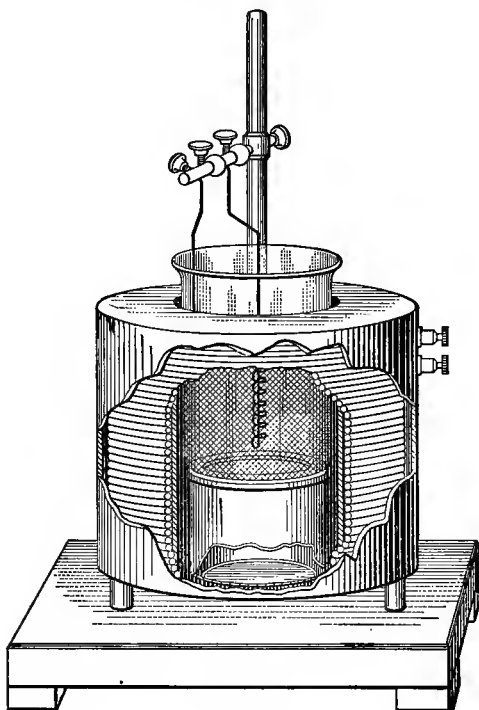
Fig. 15.

electrolyte must not extend above the cathode. The advantages claimed for this apparatus are that it is inexpensive, practically indestructible, noiseless and needs no attention.

Frary has also devised a special apparatus for

use with a mercury cathode in which the same principles are made use of (see Zeits. f. Electrochem., XIII, 308, and J. Am. Chem. Soc., Nov., 1907).

Rapid Deposition of Metals Electrolytically by Agitating the Solution with Compressed Air. — While compressed air has been used for some time, commercially, to agitate copper sulphate in the electrolytic refining of copper, so far as the writers are aware it has not been used in chemical analysis.

The writers, using the platinum electrodes as described under Babbitt metal, have deposited lead and copper simultaneously in an hour and a half by agitating the solution by means of a current of compressed air. The compressed air was conducted into the solution by means of an ordinary $\frac{1}{4}$-inch glass tube placed inside the small platinum cylinder which acted as the anode. A stream of air was allowed to bubble through the solution fast enough to secure good agitation but not to cause spattering. The current used was $ND/100 = 2$ amperes and 2.5 to 3 volts; temperature 20 to 30 degrees; volume of solution 150 cc.; time 1 to 2 hours. The deposits were equal in all respects to copper and lead deposited under the usual working conditions with stationary electrodes.

The advantages of agitating the solution by means of air instead of by mechanical means or by rotating the anode or cathode are that it permits any style of electrode to be used and does away with the cost of mechanical stirrers and revolving anodes or cathodes and cuts down the time of depositing 1 gram copper from fourteen to two hours.

Any laboratory having compressed air can be equipped for air agitation at the expense of a few cents for glass and rubber tubing.

Current Density. — Current density is the ratio of the current strength to the area of the electrode surfaces and a current strength of 1 ampere for 100 square centimeters electrode surfaces has been chosen as a unit. Take the following example. A cell has an electrode surface of 500 sq. cm., and a current of 6 amperes flows through the cell; then every 100 sq. cm. will receive a current of 6/5.0 ampere, = 1.2, or the current density is expressed ND/100 = 1.2. The symbol ND/100 expresses the density of the current per square centimeter of electrode surface exposed to its action. In this book the current density will always be expressed by the symbol ND_{100}.

PART II — DETERMINATION OF THE METALS

CHAPTER III

ALUMINUM

THERE does not seem to be any short direct method for the technical estimation of aluminum in alloys. The following elements interfere: iron, manganese, arsenic, phosphorus, chromium and titanium. As titanium, however, is rarely present in aluminum alloys, the methods dealing with its separation from aluminum will not be mentioned here. Aluminum is usually determined indirectly, although there are some reliable but tedious methods for its direct estimation. In the direct method it is weighed as either $AlPO_4$ or Al_2O_3. In the indirect method, the aluminum, iron and phosphorus (if present) are weighed together as oxides, the aluminum is then found by difference, after the iron and phosphorus have been determined and their weight deducted from the combined weight of the mixture of oxides. The direct method will be described here.

Gravimetric Method. — Dissolve a gram of the alloy in a mixture of 7 cc. strong nitric acid, 10 cc. of strong hydrochloric acid and 2 cc. of strong sulphuric acid, in a 6-ounce flask. Evaporate with gentle heat on the steam bath or hot plate as far

as possible, then heat over free flame until white fumes are being evolved copiously. Cool, add 100 cc. water and a little hydrochloric acid and heat to boiling until everything goes into solution. Should there be any residue filter this off and after igniting again treat in the same manner. Combine the filtrates which will contain the acid solution of the various bases present. Too much acid should not be present, therefore nearly neutralize the solution with ammonia, then acidify with hydrochloric acid, adding 5 cc. in excess. Dilute to 250 cc., heat to 90° C. and precipitate copper, arsenic and other metals of this group with a current of hydrogen sulphide. Arsenic, if present, will be precipitated last, and can be completely removed only by passing hydrogen sulphide for at least an hour or two at a temperature of 90° C. When near the end, allow the liquid to cool, keeping up a steady stream of gas until the liquid has attained room temperature. Filter and wash with water containing hydrogen sulphide. Test the filtrate to be sure all arsenic has been removed, by again passing the gas into it, at a temperature of 90° C. for an additional 25 minutes.

When the filtrate is free from metals of the hydrogen sulphide group, boil until free from hydrogen sulphide, then add a few cubic centimeters of nitric acid to the solution and boil for a few minutes to convert any iron to the ferric state. Now precipitate the aluminum as aluminum phosphate as follows (Carnot's method).[1] Neutralize the solution with

[1] A. Blair, " Chemical Analysis of Iron," Fifth Edition, page 192.

ammonia and sodium carbonate, but see that no permanent precipitate is formed, then add a little sodium hyposulphite, and when the liquid — at first violet — becomes colorless, 2 or 3 cc. of a saturated solution of sodium phosphate and 5 or 6 grams of sodium acetate dissolved in a little water. Boil the solution about three-quarters of an hour, or until it no longer smells of sulphurous acid. Filter, and wash the precipitate of aluminum phosphate, mixed with a little silica and ferric phosphate, with boiling water. Treat the precipitate on the filter with hot dilute hydrochloric acid, allow the solution to run into a platinum dish, evaporate to dryness, and heat at 100° C. for an hour, to render the silica insoluble. (If no silica is present the evaporation and heating may be dispensed with.) Dissolve in hot dilute hydrochloric acid filter from the silica, dilute to about 100 cc. with cold water, neutralize as before, add a little hyposulphite in the cold, then a mixture of 2 grams of sodium hyposulphite and 2 grams of sodium acetate, boil for one-half hour, wash and weigh as aluminum phosphate $(AlPO_4 \times 0.22195 = Al)$.

When chromium is present precipitate by means of ammonia in original filtrate, and fuse the precipitate of ferric oxide, alumina and chromic oxide with sodium carbonate and a little sodium nitrate, dissolve in water, add ammonium nitrate, boil well and filter. The chromic acid will be in the filtrate and the ferric oxide and alumina will be insoluble. Dissolve in hydrochloric acid, evaporate to dryness, dissolve in a few drops of hydrochloric acid, filter,

and dilute with cold water to 100 cc., add 2 or 3 cc. of sodium phosphate, and proceed as in the second precipitation of aluminum phosphate by Carnot's method.

Volumetric Method. — Proceed exactly as in the gravimetric method until the filtrate from hydrogen sulphide group is boiled free from hydrogen sulphide gas and the iron is oxidized by nitric acid. Then precipitate with ammonia and determine aluminum by Seamon's volumetric method given below.

The precipitate should first be thoroughly washed with a boiling solution of ammonium chloride to remove any zinc hydroxide which might be associated with the other constituents. The precipitate is then dissolved in the smallest quantity necessary to accomplish solution, of strong hydrochloric acid, using a No. 2 casserole. The filter paper is removed and rinsed with water into the casserole. Sodium peroxide, C.P., is then added to excess; from two to five grams is necessary, according to the amount of hydrochloric acid employed. The peroxide should be added gradually enough to avoid loss by spattering. The solution is then filtered and the filter washed thoroughly with boiling hot water. The filtrate will contain all of the alumina in solution as sodium aluminate.

A drop of phenolphthalein is now added and dilute hydrochloric or sulphuric acid is added until a gelatinous precipitate begins to show, being careful not to pass the point where the pink color of the indicator is destroyed. The standard solution of sulphuric acid (described later) is then run in

to exact neutralization. Should the end point be passed the determination may be saved by making alkaline with sodium or potassium hydroxide, and starting again with the acid. At the neutralization point all of the alumina is in form of a gelatinous precipitate. A measured quantity (about 50 cc.) of standard sulphuric acid is then added in excess, enough to make a clear solution on warming. A drop of methyl orange is next added and a standard solution of potassium or sodium hydroxide is then run in from a burette to determine the excess of sulphuric acid. The number of cubic centimeters of standard sulphuric acid in excess are deducted from the number of cubic centimeters of standard sulphuric acid employed and this remainder multiplied by the strength of the standard in alumina.

Solutions Required. — To obtain a standard solution of sulphuric acid in which 1 cc. will equal, approximately, 0.005 gram of alumina add 8.3 cc. of sulphuric acid of specific gravity, 1.84 to a liter of distilled water.

About thirty grams of potassium hydroxide dissolved in one liter of water will give a solution in which 1 cc. of the potassium hydroxide will be equivalent to 1 cc. of the acid. It is necessary, of course, to determine the exact relation.

The strength of the sulphuric acid in alumina is determined by dissolving 1 gram of pure potassium alum in 100 cc. of water, adding 2 grams of sodium peroxide, and treating as described above for the determination. Pure alum contains 10.86 per cent of Al_2O_3, consequently 0.1086 divided by the num-

ber of cubic centimeters of sulphuric acid found
necessary to equalize the alumina gives the strength
of the acid.

Reactions. — The method depends upon the fact
that sodium peroxide affords a perfect separation
of alumina from the other oxides of the fourth group
except zinc, owing to the formation of a sodium
aluminate, $Na_2O . Al_2O_3$, which is soluble in the
excess of sodium peroxide. As soon as the excess
of the latter is neutralized, aluminum hydroxide
separates out as a gelatinous precipitate. This is
dissolved in a known volume of hot standard sul-
phuric acid and the excess of the latter found by
titration with standard alkali.

Electrolytic Method. — If a solution of aluminum,
iron and chromium which contains an excess of
ammonium oxalate is submitted to the action of
the electric current, the ammonium oxalate is con-
verted into carbonate and the aluminum separates
as hydroxide, the chromium is converted into a
chromate, and the iron is deposited on the nega-
tive electrode. When precipitation is complete, the
liquid is poured off, boiled until it has only a weak
odor of ammonia, the aluminum hydroxide is
filtered off, ignited and weighed as Al_2O_3. $Al_2O_3 \times
0.5303 = Al$. This method is seldom used in practi-
cal work.

CHAPTER IV

ANTIMONY

Gravimetric Method. — In determining antimony the two elements which interfere and give the most trouble are arsenic and tin. Treat one gram of the finely divided alloy with 15 cc. of strong hydrochloric acid and add a little potassium chlorate from time to time. Increase the heat gradually until the alloy is perfectly decomposed. Boil the liquid to remove free chlorine, then add from 2 to 3 grams of tartaric acid and allow it to dissolve. Dilute to 450 cc. with hot water. Heat nearly to boiling and pass hydrogen sulphide through the solution until the precipitation is complete. Filter and wash with hydrogen sulphide water. If much tin is present the tin sulphide will run through the filter. This can be prevented by washing with a strong salt solution (sodium chloride). Transfer the filter containing the precipitate to a small beaker and digest it with a few cubic centimeters of a colorless solution of potassium or sodium sulphide. Dilute to about 100 cc. and wash with water containing a little sodium sulphide. The solution contains the sulphides of arsenic, tin and antimony, and the residue on the filter the sulphides of copper, lead, etc.

Acidulate the filtrate with hydrochloric acid and

allow to stand until the arsenic, antimony and tin
sulphides mixed with excess of sulphur have settled
completely.   Filter and wash with water (contain-
ing sodium chloride, if tin is present), then with
alcohol, and last with carbon disulphide to dissolve
the excess of · sulphur.   Transfer the precipitate
and filter to a small beaker, add 5 cc. strong hydro-
chloric acid and a little potassium chlorate and
warm the mixture, add a little more acid or chlorate
and heat until the precipitate is dissolved with the
exception of a few particles of separated sulphur.
When the sulphides are dissolved, dilute with 25 cc.
of water and add 2 to 3 grams of tartaric acid
to keep antimony and tin in solution.   Next add
2 to 3 grams of ammonium chloride and a slight
excess of ammonia to the solution.   If this becomes
cloudy on the addition of ammonia, add a little
more tartaric acid or ammonium chloride until it
clears up.   Now add 5 cc. of magnesia mixture
and one-third the volume of the solution of am-
monia.   Cover the beaker and allow to stand in a
cold place overnight.   The arsenic is precipitated
as ammonium magnesium arsenate.

Make the filtrate from the ammonium magnesium
arsenate slightly acid with hydrochloric acid.   Now
add 20 grams of oxalic acid dissolved in 200 cc. of
hot water, dilute to 300 to 400 cc., heat nearly to
boiling and pass a rapid current of hydrogen sul-
phide through the liquid for about half an hour.
The precipitate will contain all the antimony,
together with a small amount of tin.   Filter immedi-
ately, as on long standing more stannic sulphide

will separate. Wash with hydrogen sulphide water and dissolve the precipitate in ammonium sulphide. Pour the ammonium sulphide solution into a boiling concentrated solution of oxalic acid and pass hydrogen sulphide through the mixture while it continues to boil. Filter and wash with hydrogen sulphide. Drive off excess of hydrogen sulphide with a current of carbonic acid. Filter on a porcelain Gooch crucible, wash with water, alcohol, and finally with carbon disulphide to dissolve any free sulphur, dry carefully, heat to a temperature of 102° C. and weigh as antimony trisulphide ($Sb_2S_3 \times 0.71418 = Sb$). Some chemists prefer to convert the Sb_2S_3 to Sb_2O_4 by treating with fuming nitric acid ($Sb_2O_4 \times 0.78975 = Sb$).

Volumetric Method.[1] — Weigh one gram of the alloy in a 150-cc. flask, add 7 grams of potassium acid sulphate, 0.5 gram of tartaric acid and 10 cc. of strong sulphuric acid. Heat over a free flame (manipulating the flask in a holder) continuously at first, finally with the full heat of a Bunsen burner until any free sulphur is entirely expelled and the separated carbon is completely oxidized, leaving a clean melt with but little sulphuric acid. Allow to cool with the flask on its side, as otherwise the solidifying cake may break it. The object of the tartaric acid in the decomposition is to reduce the arsenic and antimony to the *ous* condition, thus rendering the subsequent solution of the antimony easy, and the precipitation of both metals as sulphides rapid and complete. Cool, add 50 cc. of

[1] A. H. Low, J. Am. Chem. Soc., Dec., 1906.

water, 10 cc. of strong hydrochloric acid and 2 or
3 grams of tartaric acid. Heat nearly to boiling
for a short time to dissolve everything soluble
(especially anhydrous iron sulphate), but do not
boil for fear of volatilizing some arsenic. Filter,
washing with hot water. Dilute the filtrate to
about 300 cc. with hot water, maintain the liquid
warm and pass in hydrogen sulphide. The arsenic
and antimony being in the *ous* condition are quickly
precipitated, ten minutes being usually sufficient.
Filter, washing with hydrogen sulphide water.
Rinse the sulphides into a beaker with hot water,
using as little as will suffice. Add a little colorless
potassium sulphide and water to extract the arsenic
and antimony sulphides. (Also tin sulphide, if
present.) Pour through the last filter and wash
with warm water containing a little colorless
potassium sulphide. With small amounts of other
sulphides present, one extraction will usually suffice.
Receive the filtrate in a 300-cc. flask. Add to it
about 3 grams of potassium acid sulphate and 10 cc.
of strong sulphuric acid and boil the mixture fi-
nally over a free flame, until the free sulphur is all
expelled and the greater part of the free acid also.
Allow the clear melt to cool with the flask on its
side. Cool, add 25 cc. of water and 10 cc. of
strong hydrochloric acid and water to effect com-
plete solution, then cool nearly to room temperature
under the tap. Now add 40 cc. of strong hydro-
chloric acid and pass in hydrogen sulphide. The
arsenic will be quickly precipitated, being in the
ous condition. Filter, washing flask and precipi-

tate with a mixture of 2 volumes of strong hydrochloric acid and 1 volume of water. Before filtering, moisten the filter with the acid mixture. A double filter supported by a platinum cone will not break under gentle suction. The arsenic is now all on the filter and the antimony (together with any tin) in the filtrate. Dilute the filtrate with double its volume of warm water and pass in hydrogen sulphide. Filter the antimony sulphide and wash with hydrogen sulphide water sufficiently to remove most of the hydrochloric acid. Rinse the sulphide from the filter into a beaker, add a little ammonium sulphide and warm to effect solution. Pour through the last filter and wash with water containing a little ammonium sulphide. Receive the filtrate in a 300-cc. flask. Small amounts of antimony sulphide may be dissolved directly on the filter. To the filtrate add 3 to 4 grams of pure potassium acid sulphate and 10 cc. of strong sulphuric acid. Boil as previously described to expel first the water, then all the free sulphur, and finally most of the free acid. Cool, add 50 cc. of water and 10 cc. of strong hydrochloric acid. Heat to effect solution and then boil for a few minutes to expel any possible sulphur dioxide. Finally add 10 cc. more of strong hydrochloric acid, cool under the tap. Dilute to about 200 cc. with cold water and titrate with a standard solution of potassium permanganate. Tin, if present, exists as stannic sulphate and is without influence.

Solutions Required. — The solution ordinarily used for iron titrations will answer. The iron value

multiplied by 1.0751 will give the antimony value. The oxalic acid value of the permanganate multiplied by 0.9532 will also give it.

Note. — In case the alloy cannot be decomposed with the mixture of sulphuric acid, potassium acid sulphate and tartaric acid, decompose it with nitric acid, boil off most of the nitric acid, add 10 cc. of strong sulphuric acid, 3 to 4 grams of potassium sulphate, boil to complete expulsion of the nitric acid, add a little tartaric acid, and after the carbonization continue the boiling until all organic matter has been destroyed. This will always leave the antimony and tin in the *ous* and *ic* states. From this point proceed as described above. (Other volumetric methods for determining antimony will be found in Part III of this book.)

Electrolytic Method. — Dissolve one gram of the finely divided alloy in aqua regia, evaporate to dryness, dissolve the residue in 2 or 3 cc. of water, add a concentrated solution of sodium hydroxide containing 2 or 3 grams of NaOH and then add 80 cc. sodium sulphide (sp. gr. 1.13–1.15). Filter and dilute the filtrates to 150 cc., bringing to a temperature of 35° C. and electrolyze with a current of $ND_{100} = 1.5$ to 1.6 amperes and 2.1 volts at the beginning and 1.45 near the end. The time required for the separation of the antimony is six hours (Z. f. Electrochem., 1, 291). The tin and arsenic remain in solution, the arsenic being present as arsenic acid. In using the rotating anode or cathode, to the dissolved residue from the aqua regia evaporation add 15 cc. sodium sulphide (sp. gr. 1.18) and 3 grams potassium cyanide, dilute to 70 cc. and use a current of 6 amperes and 4 volts, time 20 minutes.

CHAPTER V

ARSENIC

Gravimetric Method. — Proceed exactly as in the volumetric method for antimony, until the point where the arsenic is on the filter and the antimony (and tin, if the latter is present) are in the filtrate. Transfer the filter and precipitate of arsenic sulphide to a small beaker, add a little fuming nitric acid and, when action has nearly ceased, heat gently until the sulphur is dissolved, dilute, filter and evaporate to about 10 cc., add 5 cc. of magnesia mixture and then a volume of ammonia equal to one-half the volume of the solution. Stir the mixture vigorously from time to time and allow to stand in the cold overnight. Filter on a Gooch crucible and wash the precipitate of ammonium magnesium arsenate with a mixture of 2 parts water and 1 part of ammonia containing $2\frac{1}{2}$ grams of ammonium nitrate to 100 cc. Dry at 104° C. for half an hour, then increase the heat very gradually to redness and finally ignite strongly for a few minutes. Weigh as magnesium arsenate ($Mg_2As_2O_7 \times 0.48287 = As$).

Volumetric Method. — Dissolve the finely divided alloy in nitric acid in a platinum dish. Cover with a watch glass and heat until the alloy is dissolved or decomposed. Wash the watch glass and sides of the dish and evaporate the solution nearly to

dryness on a steam bath. It is now ready to treat
by Low's [1] modification of Pearce's method.

To the pasty residue add 5 grams of a mixture
of equal parts of dry sodium carbonate and potas-
sium nitrate. Heat the mass gradually over a
Bunsen burner to complete fusion. It is best to
use a very low flame at first and take plenty of time,
so that the mixed salts will melt and soak through
the mass before much decomposition occurs. In
this way loss of arsenic is prevented with some
alloys that tend to lose arsenic by volatilization.
Finally heat to the full power of the Bunsen burner
until thorough decomposition is effected. If a dif-
ficultly fusible crust is formed or lumps appear,
increase the heat, using the blast lamp if necessary,
until the mass is as smooth and homogeneous as
possible. If the dish or crucible is taken up in the
tongs and given a circular movement it will help
to make the mass smooth and well mixed. Cool,
extract the soluble portion by heating with water
until thoroughly disintegrated, and then filter and
wash the residue with cold water. Receive the
filtrate in a 6-ounce flask. Drop a bit of litmus
paper into the flask and then add nitric acid care-
fully until the solution is plainly acid, simply avoid-
ing a large excess, but if a precipitate has formed,
always add enough acid to dissolve it. Now add
10 cc. of a solution of silver nitrate (containing 17
grams in 500 cc. water), which will usually cause
a white precipitate of silver chloride, and then
cautiously add ammonia until if arsenic be present

[1] Low's " Technical Methods of Ore Analysis," p. 41.

a reddish precipitate first formed will redissolve and may not be observed at all. In this case the bit of litmus paper will show an alkaline reaction. Now cautiously add nitric acid (best dilute) until the red precipitate just redissolves or the litmus paper shows a slight acid reaction. To the faintly acid liquid add a few cubic centimeters of a strong solution of sodium acetate or 1 or 2 grams of the crystals. This will effect a replacement of the free nitric acid with acetic acid, and all the arsenic will be at once precipitated as silver arsenate, Ag_3AsO_4. Heat the precipitated mixture to boiling and then cool to room temperature, allowing the precipitate to settle somewhat, and filter. If the first portions run through turbid, return them to the filter once more. Test the filtrate with a little more silver nitrate and sodium acetate. Wash the precipitate with cold water until a portion of the washings show only a faint cloud when tested for silver with a soluble chloride. Now place the original flask under the funnel and dissolve the arsenate on the filter with cold dilute (1:1) nitric acid; 5 or 10 cc. will usually suffice. Wash the filter thoroughly with cold water. A white residue of silver chloride usually remains undissolved. Dilute the filtrate, if necessary, to about 100 cc., add about 5 cc. of a strong solution of ammonia-ferric alum and titrate to a permanent red tinge with a standard solution of ammonium thiocyanate, shaking well, especially at the end, to break up the clots of precipitate and free any solution held mechanically. Multiply the number of cubic centimeters required by the arsenic value

of 1 cc. to obtain the amount of arsenic in the alloy.

Solutions Required. — If the thiocyanate solution contains 7.617 grams of ammonium thiocyanate per liter, 1 cc. will equal 0.0025 gram, or 0.5 per cent of arsenic. It should be standardized carefully, either against pure silver or silver nitrate, which contains 63.51 per cent of silver. Weigh accurately about 0.5 gram of pure silver, dissolve in a little nitric acid, and dilute to about 100 cc., or instead, weigh about 0.8 gram of silver nitrate and dissolve in 100 cc. of water slightly acidified with nitric acid. In either case add a few cubic centimeters of a strong solution of ammonia-ferric alum (acidified with a little nitric acid) as an indicator, and titrate to a faint red tinge with the thiocyanate solution as described above. From the number of cubic centimeters required and the weight of silver taken, determine the value of 1 cc. in silver. The formula of the red precipitate, Ag_3AsO_4, shows that 107.93 parts of silver represent 25 parts of arsenic, and, accordingly, the arsenic value of 1 cc. of the thiocyanate from the silver solution is easily deduced from the silver value by proportion. Substances, such as molybdic and phosphoric acids, which may behave similarly to arsenic under this treatment, interfere, of course, with this method. Antimony, by forming sodium antimonate, remains practically insoluble and without effect.

Electrolytic Method. — Dissolve 1 gram of the alloy in aqua regia and evaporate to dryness. Moisten the residue with 2 to 3 cc. of water, add a

concentrated solution of sodium hydroxide containing 2 to 3 grams of NaOH and 80 cc. of sodium sulphide (1.13 sp. gr.). Filter, dilute the solution to 150 cc. and electrolyze with $ND_{100} = 1.5$ to 1.6 amperes and 2.1 volts. The antimony will be precipitated on the cathode in the metallic state. To determine the arsenic, acidify the antimony-free solution with dilute sulphuric acid, heat on the steam bath to remove hydrogen sulphide, filter and dissolve the precipitate in hydrochloric acid and potassium chlorate. Then add ammonia in excess and precipitate the arsenic acid with magnesia mixture and determine as $Mg_2As_2O_7$, exactly as described in the gravimetric method for arsenic.

CHAPTER VI

BISMUTH

Gravimetric Method. — Dissolve 1 gram of the alloy in a 6-ounce flask or a casserole with 10 cc. of strong nitric acid and concentrate the solution by boiling until a pasty mass results, but do not boil to complete dryness. Add hydrochloric acid (7 cc. is usually sufficient) and heat until the alloy is decomposed or in solution. Then add 8 cc. of strong sulphuric acid and boil until sulphuric acid fumes are being copiously evolved. Cool to room temperature, add 30 cc. of water and boil until all bismuth sulphate goes into solution. Cool, filter and wash with a 10 per cent solution of sulphuric acid. Filter as soon as possible, otherwise some basic bismuth sulphate will separate out. Dilute to 100 cc. and precipitate bismuth, copper, arsenic, antimony (and whatever lead may not have been removed as sulphate) with hydrogen sulphide. Filter and wash with dilute hydrogen sulphide. Place the precipitate and filter in a 250-cc. beaker, add a concentrated solution of potassium cyanide, using as little as possible to insure solution. Warm for a few minutes, filter and wash with hot water. Dissolve the sulphides of bismuth, lead and cadmium by placing the filter and precipitate in a 250-cc. beaker and heating

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with 10 cc. of dilute nitric acid. Add 20 cc. of water and filter, using a porcelain Gooch crucible. Wash with dilute nitric acid. Transfer the solution to a 400-cc. beaker, dilute to 300 cc. and heat to boiling. Remove the burner and drop a bit of litmus paper into the hot solution and neutralize the solution with dilute ammonia (2 parts water and 1 part ammonia). Add ammonia cautiously drop by drop until the solution becomes slightly cloudy. Then add 1 cc. of dilute hydrochloric acid and place on the hot plate for an hour. Do not let the solution boil. Filter the precipitate of bismuth oxychloride, using a porcelain Gooch crucible. Wash with hot water. Dry at 100° C. and weigh as bismuth oxychloride (BiOCl × 0.80166 = Bi). The BiOCl may be reduced to metallic bismuth by fusion with potassium cyanide. To do this, ignite the precipitate and filter paper in a porcelain crucible, cool, add five times its bulk of potassium cyanide, and fuse over the blast lamp. By continued heating the small molten globules of bismuth can be united into one large globule. After cooling, extract the melt with water and filter, using a weighed porcelain crucible. Wash first with dilute and then with strong alcohol. Dry the bismuth at 100° C., cool and weigh. When the bismuth is fused with potassium cyanide in a porcelain crucible, the latter is often more or less attacked and the reduced bismuth is contaminated with the material of the crucible. This error can be avoided by dissolving the bismuth in dilute nitric acid and weighing the residue matter from

the crucible.   A platinum crucible cannot of course be employed.

Volumetric Method.[1] — The bismuth oxychloride obtained above may be dissolved in nitric acid, the hydrochloric acid removed by boiling down once or twice, adding nitric acid each time.   The resulting solution, containing the bismuth nitrate, must be free from hydrochloric acid, as the basic bismuth oxalate to be subsequently titrated with permanganate is readily soluble in hydrochloric acid.   The solution should contain just sufficient nitric acid to prevent precipitation of the basic bismuth nitrate before oxalic acid is added.   Add oxalic acid in considerable excess, shake the solution and precipitate thoroughly and let settle.   Filter and boil the precipitate for from five to ten minutes with successive quantities of about 50 cc. of water.   The precipitate will be transformed into the basic bismuth oxalate.   As soon as the supernatant liquid ceases to show an acid reaction, the transformation is complete.   Dissolve the basic salt in as little dilute hydrochloric acid as possible.   Dilute the solution to 600 cc. and titrate with a $N/20$ permanganate solution.   The per cent of bismuth is calculated from the weight of oxalic acid used.   One molecule of oxalic acid corresponds to one atom of bismuth, or the oxalic acid value of the permanganate multiplied by 1.6508 gives its bismuth value.

Electrolytic Method with Fixed Electrodes. — The electrolytic precipitation of bismuth is not very successful except when small amounts are present,

[1] Sutton, " Volumetric Analysis," p. 174.

due to the spongy form of the deposit and the tendency toward the separation of some bismuth as peroxide on the anode. The best method is that used by Kammerer.[1] Proceed exactly as in the gravimetric determination until the bismuth sulphide has been dissolved in dilute nitric acid. Add 3 cc. of sulphuric acid (sp. gr. 1.84) and evaporate until white fumes are freely given off. Cool, add 30 cc. of water and 1 cc. nitric acid (sp. gr. 1.42) and heat until bismuth sulphate is dissolved. Now add 1 gram of potassium sulphate, dilute to 150 cc. and electrolyze with a current $ND_{100} = .02$ ampere, volts $= 1.8$, temperature $= 45°$ to $50°$ C., time $= 6$ to 7 hours. The current should be increased the last hour to 0.15 ampere. Heat is absolutely essential in order to get a bright metallic deposit of bismuth. Wash without interrupting the current. Dry and weigh as metallic bismuth. As much as 0.15 gram of bismuth has been separated under these conditions.

With Rotating Anode or Cathode. — Use a solution of the nitrate containing 1 cc. of nitric acid (sp. gr. 1.42) and a current of $ND/100 = 1$ ampere and 2.5 volts. Time, twenty minutes for 0.5 gram of metal.

[1] Smith, "Electro-Analysis," p. 97.

CHAPTER VII

CADMIUM

Gravimetric Method. — Dissolve one gram of the finely divided alloy in 10 cc. nitric acid (sp. gr. 1.42) in a 6-ounce flask or a casserole. Then add 8 cc. of sulphuric acid (sp. gr. 1.84) and evaporate until the white sulphuric acid fumes are freely evolved. Cool, add 30 cc. of water, heat to boiling and keep hot until any iron sulphate dissolves. Cool, filter and wash with a 10 per cent sulphuric acid solution. Dilute somewhat and saturate the solution with hydrogen sulphide water. Digest the precipitate with a strong solution of potassium or sodium sulphide. Filter and wash with dilute alkali sulphide. Dissolve the sulphides of copper, cadmium, bismuth, etc., in dilute nitric acid, add dilute sulphuric acid and evaporate until fumes of the latter appear, filter to remove any possible lead as sulphate. Wash with 10 per cent sulphuric acid solution. Then nearly neutralize the solution with potassium hydroxide, add sodium carbonate and potassium cyanide, filter and wash. To the filtrate add more potassium cyanide (just enough to keep copper in solution) and potassium sulphide and filter off the precipitate of cadmium sulphide. Wash with dilute hydrogen sulphide water. Dissolve in hot dilute hydrochloric acid (1:1). Heat to boiling, add 25 cc. of nitric acid and boil to oxidize

sulphur. Cool, add 50 cc. of a 10 per cent solution of sodium ammonium hydrogen phosphate. Neutralize with ammonia, using litmus as an indicator, add a drop or two in excess and then acidify with 1 cc. of acetic acid. Test to make sure the solution is acid. Heat (but do not boil, as the precipitate will cause bumping) for one hour, when the precipitate will become granular and settle. Filter, using a platinum Gooch crucible, and wash with hot water. Ignite, gently at first, then for a few minutes at a low red heat. Cool and weigh as $Cd_2P_2O_7$ ($Cd_2P_2O_7 \times 0.55946 = Cd$).

Volumetric Method. — Proceed as described above until the cadmium sulphide obtained is dissolved in dilute hydrochloric acid and the sulphur oxidized with nitric acid. Then add ferric chloride and citric acid and make just alkaline with ammonia. Heat to boiling and titrate with a standard solution of potassium ferrocyanide containing 12 grams to the liter, using a 15 per cent solution of uranium acetate as an outside indicator. Instead of adding ferric chloride and citric acid a drop or two of litmus solution may be added and the solution of cadmium nitrate made slightly alkaline with ammonia, then faintly reacidify with hydrochloric acid. Next add an excess of 3 cc. of strong acid. Dilute to 250 cc., heat nearly to boiling and titrate with a standard solution of potassium ferrocyanide as described in the paragraph below.

Solutions Required.[1] — Make up a solution of potassium ferrocyanide containing 12 grams of

[1] Low's " Technical Methods of Ore Analysis," p. 209.

the crystallized salt to the liter. Weigh out carefully 0.2 gram of pure cadmium or an amount of cadmium salt containing a known quantity of cadmium and dissolve in 10 cc. of strong hydrochloric acid (sp. gr. 1.20) in a covered 400-cc. beaker. Dilute to about 100 cc., add a drop or two of litmus solution as an indicator, and make faintly alkaline with ammonia. Again acidify with hydrochloric acid and then add an excess of 3 cc. of strong acid. Dilute to 250 cc. and heat nearly to boiling. Titrate the hot liquid with the ferrocyanide solution as follows: Pour off about one-third of the cadmium solution and set it aside in a beaker. Titrate the remainder by running in the standard a few cubic centimeters at a time until a drop tested on a porcelain plate with a drop of a 15 per cent solution of uranium nitrate shows a brown tinge. Now add the greater part of the reserved portion and continue the titration more cautiously until the end point is again passed. Finally add the last of the reserved portion, and to save rinsing out the beaker, pour a large part of the solution back into it again, then empty it once more. From this point finish the titration very carefully, ordinarily by testing after each addition of two drops. When the final brown tinge is obtained note the reading of the burette, then wait a minute or two and observe if one or two of the preceding tests do not also develop a color. The end point is always passed by a test or two, and the burette reading must be corrected accordingly. A further correction must be made for the amount of ferro-

cyanide required to produce a color under the same conditions when no cadmium is present. This is usually 1 drop. One cubic centimeter of the standard solution usually is equal to about 0.005 gram of cadmium.

Electrolytic Method with Fixed Electrodes. — Proceed exactly as in the gravimetric method until the cadmium sulphide is dissolved in 1:1 hydrochloric acid. The solution should not exceed 80 cc. Transfer to a 200-cc. electrolytic beaker, add a drop of phenolphthalein and then pure sodium or potassium hydroxide solution until a permanent red color is obtained. A strong solution of pure potassium cyanide is then added with constant stirring until the precipitate of cadmium hydroxide is completely dissolved. Avoid using an excess of the potassium cyanide. Dilute the solution to 150 cc. and electrolyze with a current of $ND/100 = 0.5$ to 0.7 ampere and 4 to 5 volts. Time from 6 to 12 hours. Wash the electrodes with distilled water and then with alcohol. Dry at 100° C., cool and weigh. The increase is metallic cadmium. The solution should always be tested for cadmium. Acidify with hydrochoric acid (under the hood, as fumes of hydrocyanic acid are very poisonous) and warm until the hydrocyanic acid is all driven off. Then test with hydrogen sulphide water. A yellow color or precipitation shows the presence of cadmium.

With Revolving Anode or Cathode. — To the solution of the chloride add 3 grams of pure potassium cyanide and 1 gram of pure potassium or

sodium hydroxide. Dilute to 125 cc. and electrolyze with a current of $ND/100 = 5$ amperes and 5.5 volts. Time, twenty minutes for 0.5 gram of cadmium. This is a very rapid and accurate method for determining cadmium.

CHAPTER VIII

COPPER

Gravimetric Method. — Dissolve 1 gram of the finely divided alloy in a 6-ounce flask or casserole in 10 cc. of strong nitric acid and boil gently, best over a free flame, until the greater part of the free acid has been removed. Now add 8 cc. of sulphuric acid (sp. gr. 1.84) and boil until sulphuric acid fumes are being freely evolved. Cool, add 30 cc. of water, heat to boiling and keep hot until soluble sulphates have dissolved. If any silver is present, precipitate it with a single drop of strong hydrochloric acid. Filter into a beaker and wash the flask and filter thoroughly with cold water, nearly neutralize the filtrate with ammonia and add 10 to 15 cc. of either strong sulphurous acid or ammonium bisulphate. Heat first to boiling and add from 5 to 10 cc. of a 10 per cent solution of ammonium thiocyanate, according to the amount of copper present, stirring constantly, until the greenish precipitate of cupric and cuprous sulphocyanate has become pure white. Allow to settle for ten minutes, filter on a weighed porcelain Gooch crucible and wash with hot water until the ammonium thiocyanate is completely removed, which may be determined by testing on a porcelain plate with a solution of a ferric salt, as shown by a red

coloration being no longer produced. Then wash
with 20 per cent alcohol, dry at 120° C. and weigh
as copper sulphocyanide $(Cu_2(CNS)_2 \times 0.52260 = Cu)$.

Volumetric Method. — *Iodate Method of Jamieson, Levy and Wells.* (J. Am. Chem. Soc., XXX, 5,
760.) The process to be described is based upon
the titration of cuprous thiocyanate with potassium
iodate solution in the presence of a large excess
of hydrochloric acid. This method of titrating a
number of reducing substances, such as free iodine,
iodides, arsenites and antimonites, in a very satis-
factory manner is due to L. W. Andrews. The
reaction depends upon the formation of iodine
monochloride and the disappearance of the iodine
color imparted to an immiscible solvent, such as
chloroform or carbon tetrachloride.

Cuprous thiocyanate is oxidized by iodine chlo-
ride sharply and quantitively with the formation
of cupric salts, sulphuric and hydrocyanic acids,
according to the equation $4\,CuSCN + 7\,KIO_3 + 14\,HCl = 4\,CuSO_4 + 7\,KCl + 7\,ICl + 5\,H_2O$.

Method of Analysis. — To 0.5 gram of alloy in a
6-ounce flask, add 6 to 10 cc. of strong nitric acid,
and boil gently, best over a free flame, keeping the
flask in constant motion and inclined at an angle
of about 45 degrees, until the larger part of the acid
has been removed. If this does not completely
decompose the alloy, add 5 cc. of strong hydro-
chloric acid and then continue the boiling until the
volume of liquid is about 2 cc. Now add gradu-
ally and carefully, best after cooling somewhat,

6 cc. of strong sulphuric acid, and continue the boiling until sulphuric acid fumes are evolved copiously. Allow to cool, add 25 cc. of cold water, heat to boiling and keep hot until the soluble sulphates have dissolved. Filter into a beaker and wash the flask and filter thoroughly with cold water. (With alloys containing appreciable amounts of silver a few drops of hydrochloric acid should be added before making this filtration, but not enough to dissolve any considerable amounts of the lead sulphate or antimonic oxide that may be present.) Nearly neutralize the filtrate with ammonia and add 10 to 15 cc. of strong sulphur dioxide water. Heat just to boiling and add 5 to 10 cc. of a 10 per cent solution of ammonium thiocyanate, according to the amount of copper present. Stir thoroughly, allow the precipitate to settle for 5 or 10 minutes, filter on paper, and wash with hot water until the ammonium thiocyanate is completely removed.

Place the filter with its contents in a glass-stoppered bottle of about 250 cc. capacity, and by means of a piece of moist filter paper transfer into the bottle any precipitate adhering to the stirring rod and beaker. Add to the bottle about 5 cc. of chloroform, 20 cc. of water and 30 cc. of concentrated hydrochloric acid (the two last named liquids may be previously mixed). Now run in standard potassium iodate solution (made by dissolving 11.784 grams of potassium iodate in 1 liter of water, 1 cc. = 0.002 gram Cu), inserting the stopper and shaking vigorously between additions. A violet color appears in the chloroform, at first increasing and

then diminishing, until it disappears with great sharpness. The rapidity with which the iodate solution may be added can be judged from the color changes of the chloroform.

In order to make another titration it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds or three-fourths of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation, add enough properly diluted acid to make about 50 cc. and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly colored with iodine as soon as the cuprous thiocyanate is added, but this makes no difference with the results of the titration.

The potassium iodate solution is perfectly stable and can be preserved without change for years, if protected from evaporation. Ordinarily it is unnecessary to standardize the solution, except by weighing out a known amount of the salt and dissolving it in a known volume. However, should there be any uncertainty in regard to the purity of the salt, or in connection with its relations of the volumetric apparatus, it would be advisable to standardize with pure copper, putting it through all the operations of the process, and thus eliminating also any slight constant errors.

Iodine Method. — *Determination.* Dissolve 0.5 gram of alloy in 2 cc. of nitric acid, 3 cc. of hydrochloric and 4 cc. of sulphuric acid. Evaporate to copious white fumes. Cool and take up with 25 cc.

of cold water. Add a piece of sheet aluminum and boil until all the copper is precipitated. Add 10 cc. of hydrogen sulphide water to insure complete precipitation of the copper.[1] Filter, washing three times by decantation. Pour 55 cc. strong nitric acid over the aluminum and copper. Remove the aluminum and wash with a minimum of hot water. Place the beaker under the filter and pour strong bromine water over it to dissolve any copper or sulphide of copper that may have run over. Wash with hot water and evaporate the solution to 2 or 3 cc. Add 5 cc. of hot water, 6 cc. of strong ammonia, and boil. Add 8 cc. of acetic acid and 10 cc. of the potassium iodide solution. Shake until all of the copper is precipitated and titrate.

Solutions. — 1. A solution of sodium thiosulphate; 20 grams of the salt in one liter of water.

2. A solution of starch; made by shaking one gram of finely powdered starch in a few cubic centimeters of water and pouring it into 200 cc. of boiling water. This should be made fresh every few days.

3. A solution of potassium iodide containing 300 grams to the liter.

Standardization. — Dissolve 0.2 to 0.5 gram of copper foil in 5 cc. of nitric acid and evaporate to 2 or 3 cc. Add 5 cc. of hot water and 6 cc. of

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[1] The copper is not generally precipitated completely by aluminum, hence the need of hydrogen sulphide water. Arsenic and antimony are precipitated by the hydrogen sulphide water, and are oxidized by bromine, otherwise the results would be high.

ammonia. Boil a few minutes and cool. Dilute to 75 or 80 cc., add 8 cc. of acetic acid and 10 cc. of the potassium iodide solution. Shake until all the copper is precipitated and titrate the free iodine as follows: The thiosulphate is run in until the brown of the iodine changes to yellow; then add 4 or 5 cc. of the starch solution and carefully run in more thiosulphate until the blue caused by the starch disappears, when the titration is finished.

Cyanide Method. — *Determination*. Dissolve 0.5 gram of alloy in 10 cc. of a mixture of equal parts nitric, hydrochloric and sulphuric acids, all of them concentrated. Evaporate to copious white fumes. Cool and dilute with 25 cc. of cold water. Add a piece of sheet aluminum and boil until all the copper is precipitated. This usually requires five or ten minutes. Add 10 to 15 cc. of hydrogen sulphide water and decant the solution through a filter, washing the deposited copper and the aluminum three or four times with dilute hydrogen sulphide water by decantation. Pour 10 cc. of dilute acid (1:1) over the aluminum and copper and warm slightly. Remove the aluminum and wash with a minimum of hot water. Place the beaker under the filter and pour through the latter 5 cc. of bromine water. Dilute to 125 cc., add 10 cc. of strong ammonia, cool under the tap and titrate against the potassium cyanide solution.

Solutions. — Dissolve 16 grams of pure potassium cyanide in distilled water and dilute to 1000 cc. This solution should be preserved from light in a well-stoppered bottle. One cubic centimeter

of this solution should represent approximately 1 per cent copper when a ½-gram sample is used.

Standardization. — Dissolve about 0.2 gram of pure copper foil, after weighing accurately, in 5 cc. of nitric acid, and when action ceases, dilute to 25 or 30 cc. and add 5 cc. of strong bromine water. Boil until the yellow color of bromine disappears, and then add 50 cc. of cold water and 10 cc. of strong ammonia. Cool by placing under the tap and titrate against the standard cyanide solution, until the blue color of the solution is discharged. The cyanide solution should be restandardized every day or so.

Electrolytic Method. — Dissolve 1 gram of the finely divided alloy in 10 cc. nitric acid (sp. gr. 1.42) in a 6-ounce flask. Then add 8 cc. of sulphuric acid (sp. gr. 1.84) and boil, best over a free flame, until the white sulphuric acid fumes are freely evolved. Cool, add 30 cc. of water, heat to boiling and keep hot until soluble sulphates have dissolved. If any silver is present, precipitate it with a single drop of strong hydrochloric acid. Cool, filter and dilute the filtrate to 250 cc. and saturate with hydrogen sulphide gas. Filter and wash with hydrogen sulphide water. Digest the precipitate with a strong solution of potassium or sodium sulphide. Filter and wash with dilute alkali sulphide. Dissolve the sulphides of copper, cadmium and bismuth in dilute nitric acid. Nearly neutralize the solution with potassium hydroxide, add sodium carbonate and potassium cyanide. Filter off the bismuth and wash with hot water. All the

copper should now be in the filtrate. Transfer
to a 400-cc. beaker and add 10 cc. of strong nitric
acid (do this under the hood, as the hydrocyanic
acid fumes are poisonous) and boil until hydro-
cyanic acid is completely driven off. Then filter
the solution into a 200-cc. electrolytic beaker (this
beaker is 100 mm. in height and 55 mm. in diam-
eter), and to the filtrate add a mixture of 4 cc.
strong nitric acid and 1 cc. strong sulphuric acid.
The writers have found that this mixture gave
better results than either the nitric or sulphuric
acids alone. Connect with the electrodes. The
base of the cathode should be about $\frac{1}{4}$ of an inch
from the bottom of the beaker, and the liquid should
be diluted so that the solution is about $\frac{1}{4}$ of an inch
above the top of the cathode. The electrodes used
by the writers are a cathode consisting of a plain
platinum cylinder 2 inches long and 1 inch in diam-
eter, riveted to a stout platinum wire 4 inches long,
making the total length of the cathode 6 inches.
It weighs about 14 grams. The anode is a stout
platinum wire, No. 16 gauge, with the end coiled
in a spiral. Cover the beaker with split watch
glasses to prevent loss by spattering. Connect the
electrodes and electrolyze with a current of ND/100
= 0.5 ampere and 2.5 volts. Volume of solution
125 to 150 cc., temperature 20° to 30° C., time
fourteen hours. As soon as the solution becomes
colorless wash down sides of beaker and watch
glasses with a jet of distilled water from a wash
bottle. At this point a great many authorities
direct that the beaker be filled up a little and the

current allowed to run for a half hour, and if no copper shows up on the freshly exposed platinum the deposition is complete. The writers have found that this is not the case, particularly in concentrated solutions, and that even after the solution is colorless the last traces of copper are not removed for some time until hydrogen is given off from the cathode. The complete deposition of copper may be proved by testing 1 cc. of copper solution on a porcelain plate with strong hydrogen sulphide water. If no distinct brown or yellow coloration appears the copper is completely removed from the solution.

Benner recommends the use of gauze electrodes and states that it has been found that it is possible, by means of the gauze electrode (Stoddard, J. Am. Chem., 31, 385, 1909; Chem. News, 99, 292), to deposit copper nearly as rapidly as with the rotating anode. This gives an apparatus which is as simple as and costs no more than that in ordinary use, and yet will give results with a rapidity nearly equal to those obtained with the more complicated and costly pieces. A description of the gauze electrode will be found on page 30.

The Method used follows. — From 0.5 to 1.0 gram of the alloy, when this contains interfering elements, is dissolved in nitric acid, or nitric and hydrochloric acids. When aqua regia is used, or if lead is present, sulphuric acid is added and the evaporation continued until the heavy white fumes of sulphuric anhydride are evolved. The excess of sulphuric acid is neutralized with ammonia and 3 cc. of concentrated nitric acid added. If sulphuric

acid is not added it is only necessary to concentrate to three cubic centimeters. In either case the solution is diluted to 75 cc., transferred to a tall battery beaker without being filtered (if the residue does not settle it is better to filter) and the copper deposited by means of a current of 8 to 10 amperes and 3 to 4 volts. If the deposit is black or dark colored it is dissolved in nitric acid and redeposited in the same way. This redeposition is, as a rule, easier and quicker than filtering.

The following will illustrate the accuracy of the procedure: Elements which interfere, and at the same time are likely to occur in alloys, are arsenic, antimony, lead and bismuth. The separation of antimony and bismuth from copper was tried under the preceding conditions but without success. Lead in such quantities that it will deposit with the copper is best removed as the sulphate. Arsenic in small quantities usually found in alloys will not deposit with the copper, but in amounts about equivalent to the copper present begins to be deposited with the last of this.

The removal of the interfering elements by chemical means can be accomplished by the following method. The alloy is disintegrated with nitric and hydrochloric acids, five or six cubic centimeters of sulphuric acid added and then it is evaporated until heavy white fumes of sulphuric anhydride are given off. It is now diluted with water, to one hundred and fifty cubic centimeters, boiling to insure complete solution of the basic sulphate of iron (a few drops of hydrochloric acid are added if silver

is present), filtered and washed with water containing a little sulphuric acid. The lead and silver remain on the filter paper. The filtrate is now heated to boiling and saturated with hydrogen sulphide, allowing the solution to cool during the process. The precipitated copper sulphide is filtered off and washed with water containing hydrogen sulphide. The precipitated sulphides are rinsed from the filter paper into a beaker, using as little water as possible, warmed with a little colorless sodium sulphide to remove the antimony and arsenic and again passed through the same filter, being washed with water containing some sodium sulphide. Bismuth is now removed from the copper by warming the mixed sulphides with a solution of potassium cyanide made alkaline with ammonia. This dissolves the sulphide of copper, leaving that of bismuth insoluble. The solution of the copper is boiled with nitric acid to destroy the potassium cyanide and electrolyzed in the usual manner.

CHAPTER IX

IRON

Gravimetric Method. — Treat 1 gram of the finely divided alloy in a 6-ounce flask with 10 cc. strong nitric acid and boil until decomposition has ceased and red fumes are no longer given off. If the alloy is still undecomposed add 5 cc. of strong hydrochloric acid and continue to heat the solution for a few minutes. Now add 6 cc. of strong sulphuric acid and boil over a free flame until the sulphuric acid fumes are being freely given off. Cool, add 30 cc. of cold water and heat until any anhydrous ferric sulphate is entirely dissolved. Then filter off lead sulphate. Wash with cold 10 per cent sulphuric acid. Dilute the filtrate to 200 cc. and saturate with hydrogen sulphide gas. Filter off the precipitated sulphides of copper, tin, antimony, arsenic, lead, cadmium, etc., and wash with dilute hydrogen sulphide water. Boil the filtrate from the hydrogen sulphide precipitate until this gas is entirely removed. If sulphur has separated filter it off. Now add some strong nitric acid and boil for a few minutes to convert the ferrous into ferric salts. Neutralize the solution with ammonia until a reddish brown coloration is formed, then add sodium or ammonium acetate until the color becomes a deep brown. Now add a solution of alkali succinate, after which warm the

mixture gently, allow to cool, filter on a platinum Gooch crucible and wash first with cold water, then with warm water containing ammonia, until twenty drops of the filtrate leaves no residue when evaporated to dryness on platinum. The washing with the ammonia changes ferric succinate to ferric hydroxide, which is then ignited and weighed as ferric oxide ($Fe_2O_3 \times 0.69943 = Fe$). If aluminum is present, dissolve the unignited precipitate in strong hydrochloric acid. Then treat the solution with pure potassium hydroxide solution until strongly alkaline, boil, dilute with hot water and filter. The precipitate contains the iron as hydroxide, and the aluminum exists as aluminate in the solution. If the precipitate is large, dissolve it in hydrochloric acid and reprecipitate with potassium hydroxide. Place a 400-cc. beaker under the funnel. Dissolve the ferric hydroxide in hydrochloric acid and add a spoonful of ammonium chloride, heat to boiling, and precipitate with a slight excess of ammonia. Filter on a platinum Gooch crucible and ignite to constant weight in the full heat of an Argand burner. If heated over a blast lamp there is danger of forming some Fe_3O_4.

Volumetric Methods.—*With Permanganate.* The two standard methods employed in the volumetric estimation of iron are the permanganate and dichromate methods. One is as exact as the other. The permanganate is more generally employed, and is also very convenient in titrating other elements. The permanganate solution will keep indefinitely, if protected from dust and reducing vapors. It is best

kept in glass-stoppered bottles in a dark closet.   In
determining iron by titrating with permanganate
the iron is oxidized from the ferrous to the ferric
state according to the following equation:

$$2 \, KMnO_4 + 10 \, FeSO_4 + 8 \, H_2SO_4$$
$$= K_2SO_4 + 2 \, MnSO_4 + 5 \, Fe_2(SO_4)_3 + 8 \, H_2O.$$
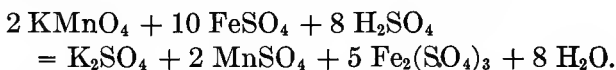
Therefore it takes 316.3 parts of potassium per-
manganate to oxidize 559 parts of iron from the
ferrous to the ferric state.

Method of Analysis. — Dissolve 1 gram of the
finely divided alloy in a 6-ounce flask with 10 cc.
of strong nitric acid and boil until most of the nitric
acid is driven off.   If the alloy is still undecomposed
add 5 cc. of strong hydrochloric acid and continue
to heat the solution for a few minutes.   Then add
6 cc. of strong sulphuric acid and boil over a free
flame until the sulphuric acid is nearly driven off.
Cool, add 10 cc. of water and 10 cc. of strong
hydrochloric acid and heat to boiling until all
soluble salts are in solution.   Dilute to 40 cc. with
cold distilled water.   Now add 2 grams of alumi-
num and reduce the iron from the ferric to the
ferrous condition, exactly as in the standardization
of the potassium permanganate.   As soon as all
the iron is in the ferrous condition add 10 cc. of
strong sulphuric acid and 20 cc. of water to give a
sharp end point.   When all action on the aluminum
has nearly ceased, fill the flask up to the neck with
cold distilled water, pouring it against the side so
that the two liquids do not mix.   Cool under the
tap.   The black residue contains lead, copper,

arsenic, etc., from the alloy. Filter off this residue
on a plaited filter, as otherwise it might consume
some permanganate. Receive filtrate in an 800-cc.
beaker. Wash the flask and filter well with cold
distilled water. Dilute to 700 cc. and titrate with
permanganate exactly as described in the standard-
ization method. Read the burette. The number
of cubic centimeters used less the correction already
determined in the standardization multiplied by the
value of 1 cc. will give the amount of iron present.
The writers use the following method. Dissolve 1
gram of the finely divided alloy in a 250-cc. beaker
with 10 cc. of strong nitric acid or with aqua regia
if necessary. When solution is complete add two
spoonfuls of C. P. ammonium chloride, heat to
boiling and precipitate with excess of ammonia.
Filter into a 400-cc. beaker, wash with hot water,
when well washed remove beaker and place a
6-ounce flask under the funnel. Punch a hole in
the filter with a sharp-pointed glass rod, and wash
bulk of the precipitate into the flask, using as little
water as possible. Now pour on the filter a hot
mixture of 10 cc. of strong hydrochloric acid and
20 cc. of water, which will dissolve any precipitate
remaining on the filter. Wash with a little hot
water. Heat the mixture in the flask until all the
ferric hydroxide is dissolved. Concentrate by boil-
ing to 30 cc. and then reduce with aluminum and
titrate with the permanganate as described under
method of standardizing.

Solutions Required. — A decinormal solution
is generally employed. To prepare this solution

dissolve 3.16 grams of the pure crystals in distilled
water. Allow the solution to stand for twenty-
four hours in order that the organic matter present
may become fully oxidized. Filter through as-
bestos and dilute to 1 liter with distilled water.
One cubic centimeter of the N/10 solution should
contain 0.00559 gram of iron. Shake well to mix
solution thoroughly and standardize. Among the
principal standards used are metallic iron, or a ferric
chloride solution of known iron contents, ferrous
ammonium sulphate containing 14.2857 per cent of
iron, oxalic acid or sodium oxalate. Offerhaus and
Fischer in the *Chemical Engineer*, Vol. IX, Feb-
ruary, 1909, show that " Sörensens " sodium oxalate
is the only suitable and unassailable standard
existing, comparing it with " Burgess " electrolytic
iron.

Metallic iron in the form of fine polished iron
wire, containing 99.8 per cent of iron, is most com-
monly used, although Treadwell[1] claims to show
that it is wrong to assign an iron value less than
100 per cent to iron wire. Claiming that the
carbides are oxidized and comparing it with elec-
trolytic iron as to its reduction value to the per-
manganate solution he finds that the impurities
have a greater reducing power than the iron itself
and that its true iron value is 100.5 per cent.
Skrobal,[2] on the other hand, contradicts Treadwell,
saying that the total oxidation of the carbides does
not take place.

[1] Treadwell's Analytical Chemistry, p. 886.

[2] Ztsch. anal. Chem., 42, p. 359.

Method of Standardizing. — Weigh into a 6-ounce flask .2 to .3 gram of wire. The wire must be perfectly free from dust or rust. If rusty, clean with fine emery cloth or sandpaper and then wipe it clean from dust and grease with a linen rag. Dissolve in 10 cc. hydrochloric acid and 20 cc. water, adding a few crystals of potassium chlorate, or in a mixture of 8 cc. of hydrochloric and 6 cc. of nitric acid. Warm gently until solution is complete. Then add 6 cc. of strong sulphuric acid and boil over a free flame until the nitric and hydrochloric acids are driven off and most of the free sulphuric acid too. Cool, then add 30 cc. of water and 10 cc. of hydrochloric acid. The iron is now ready for reduction from the ferric to the ferrous state. The principal agents used for the reduction are hydrogen sulphide, sulphur dioxide, metals such as zinc, cadmium and aluminum, and stannous chloride. The chief objection to zinc is the fact that in the presence of titanic acid the latter is reduced to Ti_2O_3, only to be oxidized again to TiO_2, by the permanganate solution, so that more permanganate solution will be required than corresponds to the amount of iron present.

The writers use metallic aluminum. W. H. Seamon[1] has the following to say as regards the superiority of aluminum over zinc and stannous chloride. It is well known, no doubt, that aluminum in warm and boiling hot solutions containing hydrochloric and sulphuric acids evolves hydrogen with great rapidity and reduces ferric salts to the ferrous

[1] Western Chemist and Metallurgist, March, 1908.

condition, but, so far as I know, its use has never been suggested for that purpose. " For more than a year I have been using it in my laboratory for the reduction of iron, comparing it, from time to time, with zinc and stannous chloride with such satisfactory results that I have abandoned the use of zinc and stannous chloride entirely, using aluminum exclusively. It is more than three times as active as zinc, as shown by the reactions:

(1) $2\,Al + 6\,HCl = Al_2Cl_6 + 6\,H,$

(2) $2\,Al + 3\,H_2SO_4 = Al_2(SO_4)_3 + 6\,H.$
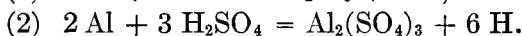
Fifty-five parts of aluminum produce six parts of hydrogen, while sixty-five parts by weight of zinc yield but two parts of hydrogen. Theoretically, one part of aluminum should reduce six parts of iron, and while I have not determined this practically, the consumption of aluminum is very small, less than one-tenth of a gram for ores carrying a high percentage of ferric iron. The reduction from sulphuric solutions is perfect and more rapid than zinc. By boiling for four or five minutes, most alloys will be completely reduced. If greater rapidity than this is desired the addition of a few cubic centimeters of hydrochloric acid will make it almost instantaneous. As a substitute for stannous chloride in the bichromate method its use will be found most satisfactory. In hot hydrochloric solutions, the reducing action is as rapid as stannous chloride and it is impossible to use an excess. The aluminum should be left in the solution while cooling down to room temperature."

Seamon's directions for using aluminum are as

follows: To the solution in the 6-ounce flask add 2 grams of pure aluminum sheet or drillings. Weigh this fairly accurately, as all aluminum contains a little iron which must be deducted from the total iron found. The reduction only takes a few minutes, and as soon as the solution is colorless the reduction may be assumed to be complete. If in doubt, test a drop of the solution on a porcelain plate with a drop of potassium thiocyanate solution. If no red tinge appears then all the iron has been reduced to the ferrous condition. The hydrochloric acid reacts as a reducing agent on permanganate as follows: $KMnO_4 + 8\,HCl = KCl + MnCl_2 + 5\,Cl + 4\,H_2O$. Sulphuric acid in a dilute solution has no bad effect on the permanganate even at a high temperature. So to the solution add a mixture of 10 cc. strong sulphuric acid and 20 cc. of water, which will serve to dissolve any remaining aluminum and also supply the necessary amount of aluminum sulphate to secure a sharp end point and entirely overcome the action of the hydrochloric acid on the permanganate. When the iron is reduced fill the flask up to the neck with cold distilled water, pouring it against the inside so that the two liquids do not mix. Cool under the tap to room temperature and filter on a plated filter, into an 800-cc. beaker or large white dish or battery jar. Wash the flask and filter well with cold distilled water and dilute to 700 cc. Run in the solution of potassium permanganate from a burette. Stir the solution carefully with a glass rod. In the first stages the color of the permanganate is de-

stroyed immediately. Towards the end a yellowish color is imparted to the solution, and the permanganate should be added carefully, drop by drop, until finally a drop of the permanganate gives a faint pink tinge to the solution. This is the end point. Read the burette. The addition of another drop should turn the liquid decidedly pink. A small correction must be applied to the burette reading to allow for the amount of permanganate used to produce a pink tint in a blank solution containing the same amount of aluminum and the same amount of acids and water used but without any iron wire. Dissolve 2 grams of aluminum in a 6-ounce flask with 10 cc. of strong hydrochloric acid and 20 cc. of water, add gradually 10 cc. of strong sulphuric acid and 20 cc. of water. When the aluminum has all dissolved, cool the flask under the tap to room temperature, filter, dilute and titrate with the potassium permanganate exactly as described in the preceding standardization. Subtract the correction thus obtained from every burette reading. The strength of the standard solution is calculated by subtracting the correction from the original burette reading and dividing the actual weight of the iron taken by the number of cubic centimeters of permanganate used.

Example:

GRAM.

Amount of iron wire weighed	.2000
Actual amount of iron present (99.8 per cent)	.1996
Original burette reading	35.70 cc.
Correction	.20 cc.
Corrected reading	35.50 cc.

35.50 cc. KMnO₄ = .1996 gram Fe.

1 cc. KMnO₄ = .00559 gram Fe.

Electrolytic Method. — Proceed exactly as described in the gravimetric method until the precipitate of ferric and aluminum succinates is converted into hydroxides by washing with ammonia. Dissolve the hydroxides on the filter with a hot mixture of 10 cc. of strong sulphuric acid and 20 cc. of water. Neutralize the solution with ammonia.[1] Assuming that 1 gram of iron may be present in the solution to be electrolyzed, 6 to 8 grams of ammonium oxalate are dissolved by heat in as little water as possible, and the iron solution is gradually added with constant agitation. It is not desirable to add ammonium oxalate solution to a ferrous solution, as difficultly soluble ferrous oxalate separates, and can be dissolved to the double salt only by long heating. With a ferric solution like the above this precaution is unnecessary. The solution is diluted to 150 cc. and electrolyzed with a current of $ND/100 = 1$ to 1.5 amperes and 3.6 to 4.3 volts at ordinary temperatures and .5 to 1 ampere and 2 to 3.5 volts at 40° to 65° C. The end of reaction is determined by testing with a solution of potassium sulphocyanate a small portion of the colorless solution strongly acidified with hydrochloric acid. When the deposition is complete wash the cathode with cold water, then with absolute alcohol, dry at 70° to 90° and weigh as metallic iron. The separated iron has a steel-gray color and adheres firmly to the cathode. With the revolving anode or cathode according to E. F. Smith,[2] 0.4922 gram of iron

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[1] Classen, "Quantitative Analysis by Elect.," p. 138.

[2] "Electro Analysis," p. 142.

will be deposited in thirty-five minutes if the following conditions are observed: Speed of anode, 800 revolutions per minute. To the ferric solution add 7.5 grams of ammonium oxalate and one cubic centimeter of a saturated solution of oxalic acid. Heat to boiling and then electrolyze with a current of $ND_{100} = 7$ amperes and 7.5 volts.

CHAPTER X

LEAD

Gravimetric Method. — Dissolve 1 gram of the finely divided alloy in a 6-ounce flask or casserole with 10 cc. of strong nitric acid and 20 cc. of water. Heat until brown fumes are no longer given off. If the alloy is not sufficiently decomposed, add 10 cc. of strong hydrochloric acid and heat the solution for a few minutes. When solution is complete, add 8 cc. of strong sulphuric acid and boil over a free flame until the white fumes of sulphuric acid are being copiously evolved. Cool, add 50 cc. of water, heat to boiling and keep solution hot until soluble sulphates have dissolved. Allow to cool, filter the lead sulphate on a weighed platinum Gooch crucible and wash with distilled water containing 10 cc. of sulphuric acid, sp. gr. 1.84, and 10 cc. of absolute alcohol to the liter.

Ignite for five minutes in the full flame of the Bunsen burner, resting the crucible on a platinum crucible cover. Cool and weigh as $PbSO_4$ ($PbSO_4 \times 0.68311 = Pb$). If there is reason to suspect the presence of silica or other insoluble matter, treat the $PbSO_4$ + silica and insoluble matter in the crucible by washing with a warm, moderately concentrated solution of sodium thiosulphate. The lead sulphate will be completely dissolved. Wash

the residue left in the crucible with hot water and
ignite for five minutes. Cool and weigh the in-
soluble matter. Subtract from the original weight
of the $PbSO_4$ + silica and insoluble matter to get
the weight of lead sulphate.

Volumetric Method. — (*W. H. Seamon's*[1] *Method.*)
(Private communication to the authors.) Weigh out
0.5 gram of the alloy into a No. 2 casserole, cover
with 10 cc. concentrated nitric acid and warm at a
temperature of from 30° to 40° C., for from ten to
twenty minutes; then add 5 cc. of strong hydro-
chloric acid and continue the warming for ten to
twenty minutes more, by which time decomposition
should be completed. Transfer to a hot plate,
evaporate to dryness at a gentle heat and avoid
spattering. Then cover with 10 cc. of concen-
trated sulphuric acid and boil hard until strong
fumes of sulphur trioxide come off. Cool to near
room temperature, add 50 cc. of water, allow the
lead sulphate to settle and filter. Keep the lead
sulphate in the casserole as much as possible and
wash twice, using 50 cc. of water each time, still
trying to keep the lead sulphate in the casserole.

Next measure out about 5 grams of sodium
acetate into the casserole, add 10 cc. of water and
2 or 3 drops of acetic acid and boil. Remove the
filtrate from under the funnel and place beneath the
latter a 125-cc. beaker. Then pour the hot solu-

[1] Chemist and Mining Engineer, Chihuahua, Mexico. Formerly
Professor of Metallurgy and Analytical Chemistry, School of Mines
and Metallurgy, Rolla, Mo., and Director of New Mexico School
of Mines.

tion of sodium acetate, after making it feebly acid
with dilute acetic acid, over the filter. Then ex-
amine the casserole, and if there should remain any
undissolved lead sulphate, add a little more sodium
acetate and boil again as before. When all of the
lead sulphate is dissolved add 10 cc. of water to the
casserole, boil and pour through the filter; repeat
this a second time. It will be found that the lead
sulphate is entirely dissolved and the bulk of the
liquid in the beaker will not be above 50 cc. Dilute
to 50 cc. if necessary, when the solution is ready
for titration.

Solutions Required. — The standard solution is
made by dissolving 4.7 to 4.9 grams chemically pure
chromate of potassium in a liter of water. Theo-
retically 4.7 grams will give a solution 1 cc. of
which is equivalent to 0.005 gram of lead. In prac-
tice Mr. Seamon states that he has found it neces-
sary to use 4.9 grams. The indicator solution is made
by dissolving 0.1 gram of silver nitrate in 100 cc. of
water. A stronger solution should not be used.

The titration may be made hot or cold, but he
advises heating the solution, for the lead precipitate
settles more rapidly. Pour off one-third of the
solution into a beaker and run in the standard
solution until a strong end reaction is obtained.
Then add the reserved portion and run cautiously
to a faint end reaction, after which mix the contents
of the two beakers by pouring from one to the other,
and finish the titration with care, allowing the lead
chromate to settle for a moment before withdrawing
the drop to be tested.

If lead is present a characteristic yellow precipitate will be formed, and the operator can with a little experience form some idea of how rapidly he may add the standard solution. The end reaction is found by removing one to two drops with a stirring rod and placing it on a color plate; then with a clean rod, which is dipped into the nitrate of silver solution, touch the drop on the plate, when a brownish coloration will be produced if there is an excess of chromate of potassium. If there is no suspended chromate of lead the end reaction is the changing of the colorless solution to a faint pink on the addition of the silver nitrate. The final reaction should always be taken after allowing the lead chromate to settle so that the drop removed should not retain the yellow color made by the lead chromate. From the burette reading deduct one-half of 1 cc. if the solution is from 50 cc. to 75 cc. in bulk; if near 100 cc. deduct 1 cc.

The standardizing of the chromate solution is best done by dissolving 1 gram of pure lead sulphate by boiling it with 40 grams of sodium acetate, 3 cc. of ammonia water and 100 cc. of water. When dissolved make feebly acid.

NOTES. — The solution should be as near neutral as possible, as the lead chromate redissolves when there is a greater excess than 3 cc. of acetic acid. The solution to be titrated should not contain salts of bismuth, barium, silver and mercury. The presence of sodium acetate is necessary and the quantity should lie between 5 and 10 grams. The lead sulphate should not be poured upon the filter paper, but should be kept in the casserole as much as possible.

Volumetric (*Molybdate Method*). — Treat exactly as described in preceding method until strong fumes of sulphuric acid are given off. Decant on the filter paper and wash by decantation 3 or 4 times with hot water containing 2 per cent sulphuric acid, then once with a little cold water. Now with the aid of a wash bottle transfer the sulphates from the filter back to the beaker, add 50 cc. of ammonium acetate and boil thoroughly. (This procedure is necessary on account of the fact that lead sulphate is not readily soluble in ammonium acetate when other sulphates such as barium and calcium are present.) Filter again through the original filter, wash with hot water and make the filtrate slightly acid with acetic acid.

The standard ammonium molybdate solution is now run in with constant stirring, testing from time to time by placing a drop of the solution upon a drop of the tannic acid solution on a spot plate. When this gives a yellow color the titration is finished.

Solutions Required. — Dissolve 8.64 grams of ammonium molybdate in water and dilute to exactly 1000 cc. Standardize as directed below. One cc. of the solution should be equivalent to 0.01 gram of lead.

To standardize, dissolve two pieces of pure lead foil weighing about 0.3 and 0.5 gram respectively in 10 to 15 cc. of 1 : 1 nitric acid. When the lead is dissolved, add 20 cc. of 1 : 1 sulphuric acid. Stir thoroughly and allow to settle. Decant on the filter paper and wash by decantation three or four

times with water containing 2 per cent sulphuric acid, always decanting as closely as possible. Wash once with a little cold water, keeping as much of the precipitate in the beaker as possible. Dissolve the lead sulphate that is on the filter paper by pouring over it 50 cc. of hot ammonium acetate solution. Pass the solution through the filter a second or third time if necessary, then wash the paper with hot water. Pour the hot ammonium acetate solution over the main bulk of the precipitate. Heat until this is dissolved; dilute to 200 cc. Make barely acid with acetic acid and titrate as above.

Ammonium Acetate. — Dissolve 200 grams of ammonium acetate in 1000 cc. of water.

Tannic Acid. — Dissolve 0.33 gram of tannic acid in 100 cc. of water.

Electrolytic Method. — Proceed exactly as described in the gravimetric method until the lead sulphate is obtained. Filter, using a 9-cm. S-S filter, No. 589. Filter with a solution of distilled water containing 10 cc. of strong sulphuric acid and 10 cc. of absolute alcohol to the liter. Wash the precipitate of lead sulphate on the filter into a 250-cc. beaker, using as little water as possible. Now add a slight excess of ammonia and warm for a few minutes. The lead sulphate is converted into porous lead hydroxide. Pour the solution slowly, a little at a time, into a 200-cc. electrolytic beaker containing 20 cc. of strong nitric acid. Stir constantly with a glass rod. Any lead sulphate not dissolved by this treatment will go into solution on being heated for a few minutes. Dilute

with distilled water. The volume of the electrolyte should be 150 cc. and its temperature 50° to 60° C. Electrolyze with a current of $ND_{100} = 1$ to 1.5 amperes and 2.5 volts.

The anodes are platinum cylinders 2 inches long and one inch wide and having a stem of heavy wire 4 inches above the cylinder, making the total height 6 inches. To obtain the best results the anodes should be roughened with the sand blast. The cathodes are heavy platinum wires 6 inches long, with spirals at the ends. In the course of an hour all the lead will have been precipitated upon the anode. Wash the latter without interrupting the current. Wash with water and alcohol and dry for fifteen minutes at 200° to 230° C. If the deposit is not dried for this length of time and at the above temperature it will weigh too much, due probably to included water, which is expelled with difficulty.

Mr. Price has found, as did Prof. E. F. Smith, that the factor to multiply the dioxide by to get the lead value should be 0.8643 instead of 0.866. The PbO_2 deposit can be readily removed by covering the anode with a solution of dilute nitric acid and inserting a rod of copper.

Mr. Price prefers the following short method.

Dissolve 1 gram of the finely divided alloy in 6 cc. of strong nitric acid and 3 cc. of water in a covered glass evaporating dish. When solution is complete, heat just to boiling, then add 50 cc. of boiling water and allow to settle. If any stannic or antimonic oxides are present, filter and wash precipitate thoroughly with hot water. To the

filtrate, or the original solution if no tin or anti-
mony was present, add 14 cc. of strong nitric
acid and electrolyze as previously described. If
manganese is present it can be completely separated
from the lead, provided the solution is kept warmed
to 70° and not more than 0.03 gram of manganese
is present in 150 cc. of solution. The current
should also be increased to 1.5 to 2 amperes and 2.5
to 2.7 volts.

Benner[1] recommends the following method for
rapidly determining lead electrolytically. The al-
loy is decomposed and the lead precipitated as
directed above by solution in nitric acid and evapo-
rated with 15 cc. of sulphuric acid. After cooling,
50 cc. of water are added and the solution boiled
until all the basic iron sulphate is dissolved. The
solution is next diluted to 200 cc., filtered and
washed free from sulphuric acid. (As much lead
sulphate as possible should be left in the beaker
and washed by decantation.) The small amount
of lead sulphate which is upon the filter is now
washed from the filter into the beaker containing
the bulk of the sulphate with the smallest possi-
ble amount of water. Ten cc. of a warm saturated
solution of ammonium carbonate is next poured
through the filter and received in the beaker con-
taining the lead sulphate. The latter is warmed
until all of the sulphate is converted to the carbon-
ate. The lead carbonate is then filtered through
the same paper, washed with water until nearly
free from ammonium carbonate, dissolved in 40 cc.

[1] J. Ind. and Eng. Chem., II, 348.

of nitric acid (1 to 3), the filter paper washed free
from lead and the solution electrolyzed in the usual
way, employing as an anode the gauze electrode
described on page 30.

Revolving Cathode or Anode. — One-half a gram
of lead can be precipitated in twenty-five minutes
if the following conditions are observed: Number
of revolutions 600 per minute.   Volume of solution
125 to 150 cc., containing 20 cc. strong nitric acid.
Current of $ND/100 = 10$ amperes and 4.5 volts.

CHAPTER XI

MAGNESIUM

TREAT 1 gram of the finely divided alloy in a 6-ounce flask or casserole with 10 cc. of strong nitric acid and heat until brown fumes are no longer given off. If the alloy is not sufficiently decomposed, add 10 cc. of strong hydrochloric acid and heat the solution for a few minutes. When solution is complete add 10 cc. more of strong hydrochloric acid and dilute to 100 cc. To the solution add ammonia in excess, then add 25 cc. of a strong bromine solution and heat to boiling. Let stand until precipitate settles, then filter through a 9-cm. S-S No. 589 filter into a 400-cc. beaker. Wash the precipitated manganese, iron, etc., with hot water. Remove filtrate and set aside. Now place a 250-cc. beaker under the funnel and punch a hole in the filter with a pointed glass rod. Wash as much of the precipitate as possible into the beaker, using as little wash water as possible. Now rinse the original flask or casserole with a hot mixture of 10 cc. of strong hydrochloric acid and 20 cc. of water, and pour it through the filter to dissolve any precipitate left on it. Wash with hot water. Heat the mixture in the beaker until everything goes into solution, and then reprecipitate with bromine and ammonia. Now filter into the 400-cc. beaker containing the first filtrate. Wash

thoroughly with hot water. If there is reason to suspect the presence of manganese in the filtrate add 10 cc. of bromine solution and heat to boiling. Filter off any manganese that is precipitated.[1] Acidify with hydrochloric acid and add 10 cc. in excess for every 100 cc. of solution. If the solution is not acid enough, zinc will be precipitated, and if too acid, lead and cadmium will be incompletely precipitated by hydrogen sulphide. Now pass in a current of hydrogen sulphide to precipitate the members of the hydrogen sulphide group. Filter and wash with dilute hydrogen sulphide water. Evaporate the filtrate in a casserole to dryness on the steam bath. Now heat until all ammonium salts are driven off. Allow to cool. The residue is dissolved in a very little dilute hydrochloric acid, the solution made barely alkaline with ammonia. Filter from any insoluble matter and precipitate the magnesium according to the methods of Gibbs or of Neubauer.[2]

Gibbs's Method. — Heat the solution to boiling and add drop by drop a solution of sodium ammonium phosphate $(NaNH_4HPO_4 + 4 H_2O)$ (160 grams of the salt dissolved in a liter of water) until no further precipitation takes place. Nearly 90 per cent of the magnesium present is at once precipitated as amorphous dimagnesium phosphate $(MgHPO_4)$:

$$NaNH_4HPO_4 + MgCl_2 = NaCl + NH_4Cl + MgHPO_4.$$

[1] Calcium is rarely, if ever, present in alloys; therefore the precipitation by ammonium oxalate is omitted here.

[2] Pages 62–64, Treadwell's "Quantitative Analysis."

The solution is now allowed to cool, after which about one-third of its volume of ammonia is slowly added with constant stirring, whereby the amorphous precipitate is at once changed to the crystalline magnesium ammonium phosphate:

$$MgHPO_4 + NH_3 = MgNH_4PO_4.$$

The 10 per cent of dimagnesium phosphate which remained in solution is also completely precipitated by this procedure as magnesium ammonium phosphate. After standing for two or three hours the supernatant solution is decanted off through a filter and the precipitate is washed three times by decantation with $2\frac{1}{2}$ per cent ammonia, finally transferred to the filter, washed completely with $2\frac{1}{2}$ per cent ammonia and dried in the hot closet. The dried precipitate is transferred as completely as possible to a weighed platinum crucible, the filter paper burned in a platinum spiral and the ash added to the main portion of the precipitate. The authors save all the time consumed in drying the precipitate, igniting the filter paper, etc., by filtering the solution through a weighed platinum Gooch crucible. In either case cover the crucible and heat, at first gently, until the ammonia is all driven off, and then more strongly and finally over the blast lamp[1] until the mass becomes snow white. By means of this ignition the magnesium ammonium phosphate is changed into magnesium pyrophosphate: $2\,MgNH_4PO_4 = 2\,NH_3 + H_2O + Mg_2P_2O_7.$

[1] It is doubtful whether it is always advisable to heat this precipitate over the blast lamp. C. Hillebrand, Bull. 176 U. S. Geological Survey, p. 66.

The crucible is cooled in a desiccator and weighed ($Mg_2P_2O_7 \times 0.21847 = Mg$). The precipitate of $MgNH_4PO_4 + 6 H_2O$ is practically insoluble in $2\frac{1}{2}$ per cent ammonia.

H. Neubauer's Method. — The slightly acid solution of the magnesium salt is treated with an excess of sodium phosphate, and then one-third of the solution's volume of 10 per cent ammonia is added with constant stirring. After standing four hours the solution is decanted through a filter and the precipitate is washed with a little $2\frac{1}{2}$ per cent ammonia. A little dilute hydrochloric acid is now poured through the filter and allowed to run into the beaker containing the magnesium precipitate and the filter is washed with water. Some ammonium chloride is now added, a few drops of sodium phosphate solution, then one-third of the liquid's volume of ammonia, and it is again allowed to stand four hours. The solution is poured through a filter, the precipitate washed three times by decantation with $2\frac{1}{2}$ per cent ammonia, transferred to the filter and completely washed with the dilute ammonia. The dried precipitate is treated as above described.

Note. — In the presence of ammonium oxalate, the precipitation of magnesium according to the above methods is complete but requires very much more time. In this case the precipitate is filtered off after standing twenty-four hours. It is preferable, however, to expel the ammonium salts by ignition. In doing this most of the zinc present is driven off as chloride and does not have to be precipitated as sulphide prior to the precipitation of the magnesium. Small amounts present will not precipitate as phosphate, being held in solution by the excess of ammonia

and ammonium chloride. The exact conditions under which a precipitate of magnesium ammonium phosphate will be contaminated have been determined by the experiments of H. Neubauer as follows. 1. If the precipitation takes place in a strongly ammoniacal solution, particularly when the phosphate solution is slowly added, the precipitate always contains some tribasic magnesium phosphate. 2. If the precipitation takes place in a neutral or slightly ammoniacal solution in the presence of ammonium salts, and ammonia is added afterwards, the precipitate then always contains monomagnesium ammonium phosphate $(Mg(\dot{N}H_4)_4(PO_4)_2)$.

To insure a pure precipitate, the solution must be neutral, as free as possible from ammonium salts, and ammonia must be added after the addition of the phosphate solution.

Electrolytic Method. — None at present known.

CHAPTER XII

MANGANESE

Gravimetric Method.—The authors use the following modification of Ford's method. Dissolve 1 gram of the finely divided alloy in a 250-cc. beaker in 12 cc. of nitric acid, sp. gr. 1.2, and evaporate the solution until it becomes sirupy. Then add 50 cc. of strong nitric acid and 5 grams of potassium chlorate and boil for ten minutes on a hot plate. Then add 25 cc. more of strong nitric acid and 5 grams of potassium chlorate and boil until yellow fumes are no longer given off. Cool, dilute with 40 cc. of water, and filter the manganese dioxide on a porcelain Gooch crucible fitted with a loose perforated disk and wash with water. Copper, zinc, nickel and tin do not interfere but large amounts of cobalt, lead and bismuth do, but this may be overcome by dissolving the precipitate in a mixture of nitric and oxalic acids, and repeating the precipitation with potassium chlorate. If lead, cobalt or bismuth are present in appreciable quantity, remove the loose disk containing the asbestos felt and precipitate, transfer to the beaker in which the precipitation was made and dissolve with 40 cc. of a mixture of strong nitric acid and oxalic acid. Pour the solution through the crucible and filtering tube, and any precipitate adhering to the

sides will be dissolved and carried into the beaker.
Now add 5 grams of potassium chlorate, boil for
a few minutes, let settle and filter into a 300-cc.
beaker.   Wash with hot water.   Transfer as much
of the precipitate as possible, by means of a jet
from the wash bottle, from the filter into a 300-cc.
beaker and then place it under the funnel.   In the
original beaker warm a mixture of 5 cc. strong
hydrochloric acid and 10 cc. of water and pour it
through the filter to dissolve any adhering ferric
hydroxide.   Wash with hot water.   Now warm the
mixture in the beaker until solution is complete,
then add 20 cc. of strong bromine water and an
excess of ammonia and heat to boiling.   Allow to
settle, filter into a 300-cc. beaker, and wash with
hot water.   Now place filter paper and precipitate
into a 250-cc. beaker and dissolve by warming with
a mixture of 10 cc. of strong hydrochloric acid and
20 cc. of water.   When solution is complete filter
from filter paper into a 400-cc. beaker.   Heat the
solution to boiling and add 20 cc. of a solution of
sodium-ammonium phosphate (160 grams of the
salt dissolved in a liter of water).   Heat to boiling,
add ammonia, drop by drop, with constant stirring.
As soon as the precipitate of ammonia manganese
phosphate begins to form stop the addition of
ammonia and stir until the precipitate becomes
crystalline.   Now add one more drop of ammonia
and stir constantly until the additional precipitate
is changed to the crystalline condition.   Continue
to add the ammonia in the same manner until the
precipitation is complete and any excess of ammonia

does not change the crystalline appearance. Add
a few drops in excess and cool in ice water, then
filter on a weighed platinum Gooch crucible and
wash with a cold 10 per cent solution of ammonium
nitrate made slightly alkaline with ammonia, until
all hydrochloric acid is removed. Ignite at first
gently until ammonia is all driven off and then
in the full flame of the Bunsen burner. Weigh
as manganese pyrophosphate ($Mn_2P_2O_7 \times 0.38702$
$= Mn$).

It is absolutely necessary in the precipitation of
the ammonium manganese phosphate to stir con-
stantly in order to convert the semigelatinous
precipitate first formed into the rose-colored, pearly
scaled crystalline form. Also if the stirring was
stopped for a minute and the precipitate allowed to
settle it would be likely to be thrown out of the
beaker, as it has a great tendency to bump.

Volumetric Method. — (*Williams's Method.*)   In
this method the manganese dioxide is precipitated
by the modified Ford method, then dissolved in
sulphuric acid with a known volume of ferrous
sulphate, and the excess is titrated by potassium
permanganate. According to the following equa-
tion it will be seen that 1 molecule of manganese
dioxide oxidizes 1 molecule of ferrous sulphate:
$MnO_2 + 2\ FeSO_4 + 2\ H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3$
$+ 2\ H_2O$. Therefore the difference between the
original amount of ferrous sulphate solution and the
excess unoxidized, as determined by titration with
permanganate, will give the amount oxidized by the
manganese dioxide.

Standard   Solutions. — (1)   Ferrous   sulphate.
Dissolve 10 grams of the pure ferrous sulphate
crystals in 900 cc. of water and 100 cc. of strong
sulphuric acid in a glass-stoppered bottle.   Keep
in a dark place free from dust, and it will preserve
its strength indefinitely.   (2) Permanganate solu-
tion. . The decinormal solution described under Iron
can be used.   According to the above equation
$2 \text{ Fe} = 1 \text{ Mn}$.   Therefore the iron factor of the
permanganate multiplied by 0.4910 will give the
factor for manganese.   One cc. $N/10 \text{ KMnO}_4$ should
equal about 0.00274 gram Mn.   Now determine the
value of the ferrous sulphate in terms of potassium
permanganate.   Run into an 800-cc. beaker from a
burette or pipette 50 cc. of ferrous sulphate solu-
tion, dilute to 700 cc. and then titrate with potas-
sium permanganate until a faint permanent pink
color is obtained.   Read the burette.   Suppose it
took 20 cc. permanganate to produce the pink tint;
then 50 cc. ferrous sulphate = 20 cc. KMnO_4 or 100
cc. of ferrous sulphate = 40 cc. of permanganate.

Method of Analysis. — Treat 1 gram of the finely
divided alloy exactly as described in the gravimetric
method until the second precipitate of manganese
dioxide is obtained on the filter free from lead,
bismuth and cobalt.   Of course, if lead, bismuth
and cobalt are not present in the original alloy the
first precipitate of dioxide is taken.   In either case
wash the precipitate well with cold water to get rid
of all the nitric acid.   Transfer the precipitate, to-
gether with the asbestos or filter paper as the case
may be, to the beaker in which the precipitate was

made. Introduce 100 cc. of ferrous sulphate solution and stir until the precipitate is all dissolved. Transfer to an 800-cc. beaker, dilute to 700 cc. and titrate with standard solution of permanganate to a pink tint. Read the burette and calculate percentage of permanganate.

Example. — 40 cc. $KMNO_4$ = 100 cc. $FeSO_4 7H_2O$ less 20 cc. $KMNO_4$ to produce pink tint leaves 20 cc. $KMNO_4$ in $FeSO_4 7H_2O$ to oxidize MNO_2. 1 cc. $KMNO_4$ = 0.00274 gram Mn. 20 cc. $KMNO_4$ = 0.05480 gram Mn. $0.0548 \times 100 = 5.48$ per cent of manganese in 1-gram sample.

Method of Metzger and McCrackan. — Place 50 cc. of the standard manganese solution in a 300-cc. Erlenmeyer flask, add 10 to 15 cc. of concentrated sulphuric acid and allow to cool. Add 1 to 2 grams of finely powdered sodium bismuthate in such a way that none of the powder sticks to the sides of the flask. Place the flask in a beaker of water so that the level of the solution is several inches below the level of the water in the beaker. Heat slowly to boiling and boil till the precipitate of basic bismuth compound settles well and has a granular appearance (about twenty minutes' boiling is usually necessary). Remove the flask and cool under running water, add a known excess of ferrous sulphate solution, dilute to about 200 cc. and titrate back with standard permanganate solution.

The manganese standard of the permanganate is calculated from the reaction, which may be represented thus:

$$Mn \cdots\cdots + 2 \ Fe \cdots \rightleftarrows Mn \cdots + 2 \ Fe \cdots$$
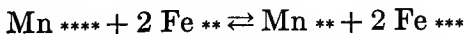
Or the value of the permanganate in terms of iron multiplied by 0.4910 gives the value in terms of manganese. The decinormal permanganate solution described under Iron may be used. 1 cc. of this will be equivalent to 0.00274 gram Mn. The ferrous sulphate solution should contain 10 grams to the liter and be frequently checked against the permanganate.

Electrolytic Method. — In a sulphuric acid solution manganese is deposited on the anode as MnO_2. When more than 0.3 gram of manganese is present results are unsatisfactory. *Method:* Treat 1 gram of the finely divided alloy in a 6-ounce flask with 10 cc. of strong nitric acid and boil until brown fumes are no longer given off. If solution is not complete add 5 cc. of strong hydrochloric acid and heat gently until solution is as complete as possible, then add 6 cc. of strong sulphuric acid and boil over a free flame until the white fumes of sulphuric acid are being evolved freely. Cool, add 30 cc. of water and boil gently, then let stand hot until all soluble salts go into solution. Filter and wash with a solution of distilled water containing 10 cc. of strong sulphuric acid and 10 cc. of absolute alcohol to the liter. To the filtrate add 1 cc. of strong sulphuric acid. Dilute to 150 cc. and electrolyze with a current of $ND_{100} = 0.5$ to 1 ampere and 2.5 volts. Temperature 60°. Time 3 hours. Use the same anodes as described under Lead. When deposition is complete, wash without interrupting the current, first with water and then with alcohol. Now dry and then ignite and weigh as Mn_3O_4 ($Mn_3O_4 \times$

$0.72027 = Mn$). Any dioxide that has become detached during either the deposition or the washing is filtered on an ashless filter and ignited in a platinum crucible, weighed and added to the weight of the Mn_3O_4 on the anode.

Revolving Cathode or Anode. — To the filtrate from lead sulphate add 1 cc. of strong sulphuric acid, dilute to 125 cc. and electrolyze with a current of $ND_{100} = 5$ amperes and 11 volts. Time 15 minutes for 0.3 gram Mn.

CHAPTER XIII

NICKEL AND COBALT

Gravimetric Method. — These elements occur together in nature and are generally separated together from interfering elements. Treat 1 gram of the finely divided alloy in a 6-ounce flask with 12 cc. of strong nitric acid and boil until the solution becomes sirupy. Then add 10 cc. of strong nitric acid and 5 grams of potassium chlorate and boil for ten minutes on a hot plate. Then add 5 cc more of strong nitric acid and 5 grams of potassium chlorate and boil until yellow fumes are no longer given off. Cool, dilute with 40 cc. of water and filter, wash with hot water, reserve filtrate. Now transfer as much of the precipitate as possible, by means of a jet from the wash bottle, from the filter into the flask, then place it under the funnel and pour through the filter a warm mixture of 5 cc. strong hydrochloric acid and 10 cc. of water to dissolve any adhering precipitate. Wash with hot water. Now warm the mixture in the flask until solution is complete, then add 20 cc. of strong bromine water and an excess of ammonia. Heat to boiling, allow to settle, filter into a 400-cc. beaker and wash with hot water. Combine the two filtrates and boil until excess of ammonia is driven off, then neutralize with hydrochloric acid and add

10 cc. in excess. Boil for a few minutes, dilute to 300 cc. and saturate with a current of hydrogen sulphide. Filter off sulphides of hydrogen sulphide group into a 400-cc. beaker, washing with dilute hydrogen sulphide water. Boil the solution to drive off hydrogen sulphide, then add 5 cc. of hydrochloric acid. Heat the nickel solution to boiling and add a 1 per cent alcoholic solution of dimethylgloxime[1] until the amount of the reagent is about 5 times that of the nickel thought to be present. A larger excess is unnecessary but can do no harm. Ammonia is then added cautiously until the solution has a faint odor. The solution is filtered while still hot through a weighed porcelain Gooch crucible, the precipitate washed with hot water and dried to constant weight at 110 to 120° C. It has the composition $C_8H_{14}N_4O_4Ni$ and contains 20.325 per cent of nickel $(C_8H_{14}N_4O_4Ni \times 0.20325 = Ni)$. It is almost completely insoluble in water and only very slightly soluble in alcohol and glacial acetic acid. Stronger acids decompose the compound with the formation of the corresponding nickel salt and the free oxime. Precipitation, filtration and washing consume less than 15 minutes and the drying of the precipitate requires only 45 minutes. The oxime is readily recovered by mixing the nickel compound to a paste with water, warming with KCN, filtering hot and precipitating the oxime at once by the addition of acetic acid. Nickel is readily separated from cobalt on account of the fact that the cobalt compound is not precipitated

[1] O. Brunck, Z. angew. Chem., 20–38, 44.

even on standing. To separate nickel from cobalt and zinc proceed as follows: To the filtrate from which hydrogen sulphide has been driven off add 5 cc. of strong hydrochloric acid and 2 to 3 grams of NH_4Cl to prevent precipitation of $Zn(OH)_2$ by the ammonia. Now dilute the solution so that 100 cc. contains not more than 0.1 gram of cobalt. More concentrated solutions tend to dissolve the precipitate. While the cobalt compound is not precipitated, it is formed in the solution, and consequently more of the reagent must be added as the proportion of cobalt increases. When solution is properly dilute, precipitate nickel as described above.

The authors use the following short method, which does away with the preliminary separation of manganese, iron, etc. Treat 1 gram of the finely divided alloy in a 6-ounce flask with 10 cc. of strong nitric acid, or whatever acids are necessary to decompose it. When solution is complete add 7 cc. of strong sulphuric acid and boil over a free flame until the white fumes are being freely evolved. Cool, add 30 cc. of water, heat to boiling, and allow to stand hot until all soluble sulphates are in solution. Cool, filter and wash with dilute 10 per cent sulphuric acid. Dilute the filtrate to 200 cc. and saturate with a current of hydrogen sulphide. Filter into a 400-cc. beaker and wash with dilute hydrogen sulphide water. Boil the solution to drive off hydrogen sulphide, then add 5 cc. of strong hydrochloric acid and 2 to 3 grams of NH_4Cl to prevent precipitation of $Zn(OH)_2$ by the ammonia and to help keep any large excess of chromium in

solution.   Now add 2 to 3 grams of tartaric acid to keep any aluminum, iron and chromium in solution. Dilute the solution so that 100 cc. contains not more than 0.1 gram of cobalt, and if any manganese is present neutralize the solution with sodium acetate instead of ammonia.   Now heat the solution to boiling and precipitate nickel with dimethylgloxime exactly as previously described.

Volumetric   Method. — (*Price's   Modification   of Moore's Method.*)   Proceed exactly as in the above gravimetric method until· filtrate free from members of the hydrogen sulphide group is obtained. Boil solution to get rid of hydrogen sulphide, then add 5 cc. of strong nitric acid and boil to oxidize any iron.   Now add 2 cc. of strong sulphuric acid, which will insure a sharp end point in the subsequent titration.

Nickel.[1] — Transfer the solution containing the iron, nickel and zinc to a 400-cc. beaker.   Add from 3 to 4 grams of ammonium chloride and then 50 to 75 cc. of a solution of sodium pyrophosphate containing from 10 to 15 grams of Merck's pure crystals.   Make up this solution just before using, and use a quantity depending upon the amount of zinc present.   Neutralize with ammonia and then add enough to make the solution only slightly but yet distinctly alkaline.   A large excess of ammonia will hinder or entirely prevent the reaction.   Cool and do not let temperature of the solution get much above 20° C., or the result will be irregular.   Add 2 cc. of a 10 per cent solution of potassium iodide

[1] W. B. Price, Chem. Eng. IX, 4.

and titrate with a standard solution of potassium cyanide containing silver nitrate, until the white cloud caused by the formation of silver iodide has entirely disappeared and one drop of the cyanide causes a clear solution.   This is the end point, which is very sharp and distinct.   The following reactions take place:

(1) $Ni(NO_3)_2 + 4\ KCN = Ni(CN)_2\ 2\ KCN$
$+\ 2\ KNO_3.$

(2) $AgNO_3 + 2\ KCN = AgCN \cdot KCN + KNO_3.$
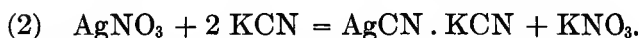
The turbid white cloud in the solution is caused by the precipitate of silver iodide, which is almost insoluble in weak ammonia, and this turbidity will increase up to the point where the formation of the double cyanide of nickel and potassium is complete, when the slightest excess of cyanide will clear up the solution.

The method of estimating nickel by means of adding potassium cyanide to an ammoniacal solution of nickel containing silver iodide in suspension, so that the solution remained turbid until the nickel was all converted into the double cyanide of nickel and potassium, after which a single drop of the cyanide in excess cleared up the solution, was originally proposed by T. Moore, and modified by Mr. Price for use in German silver, etc.

The following elements interfere with the method: manganese, zinc, iron, aluminum, and especially copper, which, owing to its forming cyanides, would render the process valueless.   Cobalt if present will be estimated as nickel.

The iron, aluminum and zinc may be kept in solution so that they do not interfere, by using organic acids, such as tartaric, citric, etc., or sodium pyrophosphate.

Solutions Required. — Standard solution of potassium cyanide containing silver nitrate. This solution should contain 25 grams of pure potassium cyanide and 1.25 grams of silver nitrate to the liter. Many of the commercial cyanides contain sulphur, which causes a darkening of the solution when titrating, due to the formation of silver sulphide. If pure cyanide is not obtainable, the sulphur impurity may be removed by thoroughly agitating the cyanide solution with oxide of bismuth. Potassium iodide, 10 per cent solution. Sodium pyrophosphate, Merck's pure crystals. Ammonium chloride, the C. P. salt.

The solution is standardized on a solution of known nickel contents. The authors use crystallized, C. P. nickel sulphate. Dissolve about 4 grams in a 400-cc. beaker. As all nickel sulphate contains iron as an impurity, the iron must be removed before electrolyzing solution for nickel. After removal of iron, transfer solution to a carefully graduated 500-cc. flask. Dilute to the mark with water and after thoroughly mixing the solution remove two 50-cc. portions with a pipette; transfer to two 200-cc. electrolytic beakers. Add 2 cc. sulphuric acid (sp. gr. 1.84), neutralize with ammonia, add 40 cc. of ammonia (sp. gr. 0.90). Electrolyze with a current of $ND_{100} = 0.5$ ampere and 2.5 volts.

After the nickel is all precipitated, wash with water and alcohol, dry and cool. The increase in weight gives the actual nickel contained in 50 cc. of solution. A solution of this strength should contain about 0.1 gram of nickel and should contain enough free acid to prevent the formation of any precipitate on the addition of ammonia to alkaline reaction. If a precipitate forms, add a little ammonium chloride and it will clear up.

Take 50 cc. of the solution in a pipette and transfer to a 400-cc. beaker, dilute to 200 cc., make slightly alkaline with ammonia, add a few drops of potassium iodide and titrate with potassium cyanide solution, adding it slowly, until one drop causes the white cloud to disappear entirely.

Example. — If 50 cc. of the solution contained 0.0905 gram of nickel and it took 20.3 cc. of potassium cyanide to produce a clear solution, then 1 cc. of potassium cyanide would be equivalent to 0.00445 gram of nickel. It is surprising that this method has not come into more general use, combining as it does extreme accuracy and great rapidity with ease of manipulation. After the removal of the copper, the total time consumed in determining the nickel should not exceed twenty-five minutes.

Electrolytic Method. — Proceed exactly as described in the first gravimetric method until filtrate free from members of the hydrogen sulphide group is obtained. Boil the solution to small bulk and nearly neutralize any acid with sodium hydroxide. Dissolve 5 grams of sodium hydroxide in 50 cc. of water and pour slowly into this, with constant stirring, the solution containing the nickel, cobalt

and zinc. Dilute the solution with an equal bulk of water and filter. Redissolve the precipitate in a little hydrochloric acid, nearly neutralize, and again pour into a solution containing 5 grams of sodium hydroxide. Dilute and filter. Dissolve the nickel and cobalt hydroxides in dilute sulphuric acid and wash the paper free from acid. Dilute to 125 cc., add 5 grams of ammonium sulphate and 40 cc. of strong ammonia and electrolyze overnight with a current of $ND_{100} = 0.5$ to 0.7 ampere and 2.8 to 3.3 volts at the ordinary temperature. When completely deposited a few drops of the ammoniacal solution tested with ammonium sulphide on a porcelain plate should show no black color or tinge.

Revolving Cathode or Anode. — One-half gram of nickel can be deposited in twenty-five minutes by observing the following conditions: Volume of solution 125 cc. containing 1.5 grams of ammonium sulphate and 30 cc. of ammonium hydroxide (sp. gr. 0.90). Electrolyze with a current of $ND_{100} = 4$ amperes and 5.5 volts.

Separation of Nickel and Cobalt with Determination of both Elements. — The nickel and cobalt are determined electrolytically, dissolved in nitric acid and then converted into the chlorides by boiling with hydrochloric acid. The solution is then diluted so that the concentration of the cobalt does not exceed 0.1 gram in 100 cc. because more concentrated solutions tend to dissolve the precipitate. The diluted solution is heated to boiling and the nickel precipitated by means of dimethylgloxime as

previously described. The cobalt is determined by subtracting the weight of the nickel from the combined weights of the nickel and cobalt.

The cobalt may also be determined directly by the precipitation with nitroso - β - naphthol, $C_{10}H_6(NOH)$.[1] Since the cobalt precipitate is very voluminous, this method is especially suitable for the determination of a small amount of cobalt in the presence of a large amount of nickel. This substance, with cobalt, forms the compound $[(C_{10}H_6O(NO)]_3Co$, cobalti - nitroso - β - naphthol, which is insoluble in hydrochloric acid, whereas the nickel compound $[(C_{10}H_6O(NO)]_2Ni$ is soluble in hydrochloric acid. Proceed exactly as described in the electrolytic method until the hydroxides of nickel and cobalt are dissolved in dilute sulphuric acid. To the solution of the sulphates add 4 to 5 cc. strong hydrochloric acid, warm, and add a hot solution of nitroso-β-naphthol in 50 per cent acetic acid as long as precipitation ensues. After the precipitate has settled, test to see if the precipitation is complete. Allow to stand for a few hours at the ordinary temperature, filter, and wash first with cold and then with warm 12 per cent hydrochloric acid until all the nickel is removed, then wash with hot water to remove all hydrochloric acid. Dry the precipitate, fold the paper, and ignite in a Rose crucible after adding a little pure crystallized oxalic acid. To avoid loss, incinerate the filter first at a low temperature, gradually increase the temperature, and finally reduce to metallic cobalt in a current

[1] Knorre and Illinski, Ber. Deutsch chem. Gesell., 1885, p. 699.

of hydrogen. Cool and weigh as metallic cobalt. Add sulphuric acid to the filtrate containing the nickel, evaporate the greater part of the acid and determine the nickel either electrolytically or volumetrically as previously described.

CHAPTER XIV

PHOSPHORUS

PHOSPHORUS is generally separated in the non-ferrous alloys as stannic phosphate and then determined by Oettel's method. In phosphor-bronzes and similar alloys there is generally sufficient tin present to retain all the phosphorus and to form stannic phosphate containing all of the phosphorus present in the alloy. If there is not enough tin in the alloy, metallic tin must be added. Experiments have proved that there should be from 5 to 8 times as much metallic tin added or present as there is phosphorus in the alloy.

Dissolve from 3 to 10 grams of the alloy (depending on the amount of phosphorus present in the alloy) in a covered casserole with strong nitric acid, and digest until it is completely decomposed and the residue is pure white. Filter the mixture of stannic phosphate and oxide and wash well with hot water. Dry the precipitate and transfer it together with the filter paper to a porcelain crucible and ignite. Cool and weigh. Now add three times as much potassium cyanide, cover the crucible, and fuse at a red heat for ten or fifteen minutes. The stannic oxide is reduced to metallic tin and the phosphoric acid unites with the potassium to form potassium phosphate. Extract the melt with hot

water, and the potassium phosphate, together with the potassium cyanate formed and the excess of potassium cyanide, will pass into solution. Filter and boil the solution with concentrated hydrochloric acid until the hydrocyanic acid is expelled. (Do this in the hood, as the fumes of hydrocyanic acid are very poisonous.) Cool and saturate with hydrogen sulphide gas to precipitate any copper and tin redissolved by boiling the solution in the presence of an excess of potassium cyanide. Filter off the sulphides of tin and copper and wash with dilute hydrogen sulphide water. Add a little bromine water to the solution and boil, to expel the hydrogen sulphide. The volume of the solution should not exceed 50 cc. at this point. Cool and to the cold solution add enough ammonia to make the solution faintly alkaline. Then add 5 cc. to 10 cc. of magnesia mixture[1] and one-half its volume of strong ammonia and stir it well. When the precipitate of ammonium-magnesium orthophosphate has begun to form, stop stirring and allow it to stand in cold water for ten or fifteen minutes, then stir vigorously several times at intervals of a few minutes and allow it to stand overnight. Filter on a small ashless filter and wash with a mixture of 2 parts water and 1 part of ammonia containing 2.5 grams of ammonium nitrate to

[1] *Magnesia Mixture.* — Dissolve 11 parts of crystallized magnesium chloride ($MgCl_2 + 6 H_2O$) and 28 parts of ammonium chloride in 130 parts of water. Add 70 parts dilute ammonia (sp. gr. 0.90). Allow the mixture to stand one or two days and filter. 10 cc. of this solution will precipitate 0.1 gram of P_2O_5.

100 cc.   Dry the filter and precipitate and ignite them at a very low temperature at first, so as to carbonize the filter without decomposing the precipitate, which may then be readily broken up with a platinum wire.   Raise the heat gradually and finally ignite in the full flame of the Bunsen burner until the residue is perfectly white.   Cool and weigh as magnesium pyrophosphate ($Mg_2P_2O_7 \times 0.27847 = P$).

Considerable time may be saved by filtering directly into a weighed platinum Gooch crucible. Heat gently at first and then to the full heat of the Bunsen burner.   Cool and weigh as before.

Any arsenic present in the alloy will be found in the phosphate of tin residue as arsenic acid.   Numerous experiments have shown that the greater part of the arsenic forms an alloy with the tin and the rest volatilizes on being fused with the potassium cyanide.   Therefore, as none of the arsenic passes into solution as potassium arsenate, this method affords a complete separation between the phosphorus and the arsenic, and there is no danger of the $Mg_2P_2O_7$ precipitate being contaminated with any $Mg_2As_2O_7$.

Messrs. W. Gemmel and S. L. Archbutt describe in the *J. Soc. Chem. Ind.*, May 15, 1908, the method which they used in determining phosphorus in a large number of samples of phosphor tin with good results.   Two to five grams of the sample were placed in a 500-cc. Jena flask fitted with a tap funnel and delivery tube.   The tap of the funnel was a " two-way," allowing gas or liquid to be

introduced as desired. The absorption apparatus consisted of three Drechsel bottles, the first two containing about $\frac{1}{4}$ inch of liquid bromine covered with bromine water to about one inch in depth, and the third bromine water only. The air was first completely removed by passing a current of carbon dioxide through the apparatus for about five minutes; 50 to 100 cc. of concentrated hydrochloric acid were then introduced and the contents of the flask gently heated. The sample dissolved readily, and it was obvious from the appearance of the first Drechsel bottle that vigorous action was taking place between the evolved gases and the bromine. When the action had practically ceased, the contents of the flask were gently boiled to effect complete solution of the tin and to expel any phosphorus hydrides in the liquid. A current of carbon dioxide was then passed through the flask for five minutes to drive forward any remaining traces of evolved gases into the Drechsel bottles. These were then disconnected, the contents rinsed into a large beaker, the bromine boiled off, and the solution concentrated. From this solution the phosphorus was precipitated in the usual manner with magnesia mixture.

The alloys used in these tests contained no arsenic, which would have been estimated along with the phosphorus, had it been present. Any appreciable quantity present in the sample should subsequently be estimated in the magnesium pyrophosphate by solution in hydrochloric acid, reduction and precipitation with sulphureted hydrogen.

Before the precipitation of the phosphorus by magnesia mixture no precipitate was ever obtained with ammonia or sulphureted hydrogen, showing that no tin had been carried over. The contents of the evolution flask were always tested for phosphorus, and nothing more than the merest trace was ever found.

CHAPTER XV

SILICA

In all alloys that are decomposed by hydrochloric or nitric acid, the silicic acid is determined by converting the soluble modification of the acid into the insoluble modification by repeated evaporations and subsequent ignition over the blast lamp. Dissolve 1 gram of the finely divided alloy in a covered 250-cc. beaker with 8 cc. of strong nitric acid. Remove the watch glass and evaporate the solution to dryness on the hot plate. Replace watch glass and increase the heat until any ferric nitrate is decomposed. Cool and add 6 cc. of strong hydrochloric acid and heat until all soluble salts are in solution. Remove watch glass, evaporate again to dryness on the hot plate and redissolve in 6 cc. of strong hydrochloric acid by heating gradually. Now add 30 cc. of water and 5 grams of ammonium chloride, which will keep any lead salts in solution. In the absence of lead omit the use of ammonium chloride. Heat to boiling to insure solution of all soluble salts. Filter on a 9-cm. ashless filter. Wash first with dilute hydrochloric acid to dissolve any ferric salts, and then with cold water. Clean the sides and bottom of the beaker by means of a rubber-tipped glass rod, and wash into the filter with cold water. Dry and

ignite in a platinum crucible. Weigh the residue. To test the purity of the precipitate and obtain the true silica, moisten the residue with water, add 10 drops of sulphuric acid and enough hydrofluoric acid to dissolve it completely, evaporate to dryness, ignite and weigh. The difference between the two weights is silica. The following method is fully as accurate and is much more rapid. Dissolve 1 gram of the finely divided alloy in a 6-ounce flask in 10 cc. of strong nitric acid and when decomposition is complete add 5 cc. of strong sulphuric acid and heat over a free flame until white fumes are being freely evolved. Continue the heating until most of the sulphuric acid is driven off. Cool, add 30 cc. of water and 5 grams of ammonium chloride if lead is present. Heat to boiling until all soluble salts are in solution. Filter hot, and wash first with dilute hydrochloric acid and then with hot water. Ignite and weigh. Treat residue as before described with sulphuric acid and hydrofluoric acid. Evaporate, ignite and weigh. Difference between two weights is pure silica.

CHAPTER XVI

SULPHUR

Dissolve 1 gram of the finely divided alloy in a 6-ounce flask with 8 cc. of strong nitric acid. Heat gently until action has ceased and until red fumes are no longer given off freely, adding from time to time a few drops of strong hydrochloric acid if it is necessary to insure complete decomposition. When solution is complete or the alloy is decomposed, add $\frac{1}{15}$ gram of dry C. P. sodium carbonate and evaporate to dryness on the hot plate, or it can be brought to dryness in less time by boiling over a free flame. The sodium carbonate will prevent any loss of sulphuric acid due to the decomposition of the sulphates at a high temperature, and it will also convert any lead sulphate to carbonate and at the same time make the combined SO_3 soluble as sodium sulphate. Cool and then add 6 cc. of strong hydrochloric acid, heat until anything soluble goes into solution and evaporate again to dryness on the hot plate to render any silica insoluble and to expel all nitric acid. Redissolve in 6 cc. of strong hydrochloric acid and evaporate until ferric chloride, etc., begins to separate out; then add 2 cc. of hydrochloric acid and 30 cc. of water and if any antimony is present add a little tartaric acid before precipitating with

barium chloride to prevent the precipitation of antimony oxide with the barium sulphate. Heat to boiling, filter and wash, taking care that the filtrate and washings do not exceed 100 cc. in volume. Heat the filtrate to boiling, add 10 cc. of a saturated solution of barium chloride and allow it to stand in the cold overnight. Filter into a porcelain Gooch crucible, wash with a little very dilute hydrochloric acid and then with cold water, ignite for five minutes in the full heat of the Bunsen burner, resting the covered crucible on a platinum crucible cover. Weigh as barium sulphate ($BaSO_4 \times 0.13738 = S$). The barium sulphate, if pure, should be white; if it is reddish in color, ferric oxide has been precipitated with the barium sulphate. Should this be the case, fuse the precipitate with sodium carbonate, dissolve in water and filter. Dissolve the residue in hydrochloric acid, reprecipitate with ammonia, weigh the ferric oxide and subtract its weight from that of the barium sulphate. In the presence of much copper the barium sulphate is contaminated with basic copper salts.

To avoid this, proceed as follows: Dissolve 1 gram of the finely divided alloy in a covered 200-cc. electrolytic beaker in 15 cc. of strong nitric acid and as soon as the alloy is decomposed dilute to 150 cc. with distilled water and electrolyze with a current of $ND_{100} = 1$ to 1.5 amperes and 1.4 volts, using electrodes consisting of two platinum cylinders one fitting inside the other. The lead will be deposited on the anode and the copper on the cathode.

When the lead and copper are removed, add a little sodium carbonate, evaporate to dryness on the hot plate and proceed exactly as described in the first method. If results are desired as soon as possible, instead of letting the solution stand in the cold overnight, keep the solution at a temperature not less than 75° C. on the steam bath or hot plate until the precipitate has completely settled, which will take place inside of three hours.

If means are not at hand for separating the copper and lead electrolytically, the fusion method may be used. Mix thoroughly 1 gram of the finely divided alloy in a large platinum crucible with 10 grams of sodium carbonate free from sulphur and ½ gram of potassium nitrate. Heat the crucible very cautiously over a blast lamp until the fusion is quiet, the last few minutes of the fusion being at the highest temperature of the blast.

If gas containing sulphur is used, the contents of the crucible must be protected from the flame gases with a suitable shield. A piece of asbestos board with a hole in which the crucible is placed in an inclined position answers the purpose very well. The fusion is completely disintegrated in hot water, to which a few drops of alcohol may be added to reduce and precipitate any manganese present. Filter and wash the residue with a 1 per cent solution of sodium carbonate. To the filtrate, which should not exceed 100 cc., add very cautiously a slight excess of hydrochloric acid. Heat to boiling and add 10 cc. of a 10 per cent solution of barium chloride. Now place the beaker on the steam bath

or hot plate until the precipitate subsides. Filter, wash with hot water until free from chlorides, ignite in an open platinum crucible and weigh as $BaSO_4 . BaSO_4 \times 0.13738 = S$.

If there is reason to suspect the presence of silica in the precipitate, the latter can be purified by the addition of a few drops of sulphuric acid and 2 or 3 cc. of hydrofluoric acid, evaporating, igniting and weighing. The difference between the two weights is pure $BaSO_4$. Some chemists prefer to use sulphur-free sodium peroxide in place of the sodium carbonate and potassium nitrate, in which case the fusion is conducted in a nickel crucible, using 5 grams of the peroxide. The rest of the treatment is the same. The 10 per cent solution of $BaCl_2$ is prepared by dissolving 100 grams of the crystallized salt in a liter of water. Ten cc. of a solution of this strength will precipitate 0.16 gram of sulphur as barium sulphate.

Determination of Sulphur in Brass and Bronze.[1] — For the determination of sulphur in brass and bronze the above method is rather circuitous. The following method is an adaptation of that used for years for the determination of sulphur in organic compounds to the making of sulphur determinations in brasses and bronzes, and has been found to give thoroughly satisfactory results.

With the aid of a mill-cut file, fine enough to make filings which will easily pass through a 100-mesh sieve, filings of the metal are prepared (file across machine face of test bar) and passed through

[1] Gustave Thurnauer, J. Ind. and Eng. Chem., June, 1910.

a sieve. Any small particles of iron from the file are removed with the aid of a magnet.

One gram of these filings is thoroughly mixed with 6 grams of a powder consisting of 2 parts of potassium chlorate and one part of sodium carbonate.

In a wrought-iron crucible there is first placed a small quantity of sodium carbonate to cover the bottom, then the mixture of the filings with the carbonate and chlorate is carefully transferred into this crucible, and finally the whole mixture is again covered over with a small quantity of sodium carbonate and chlorate. The crucible is then covered with a porcelain cover and heated first slowly and then to a fairly high temperature over a Bunsen flame, until the whole mass is thoroughly melted.

The fusion after cooling is digested with hot water. The salts, which contain all the sulphur as sulphate, are filtered from the oxide residue, the filtrate is acidulated with hydrochloric acid and boiled to remove all carbon dioxide. The solution is then neutralized with ammonia and made slightly acid by carefully adding hydrochloric acid until an acid reaction appears, and then 2 or 3 drops in excess are added. The solution is then brought to boiling and a boiling solution of barium chloride is added. By letting the solution stand for one-half hour in a warm place, but not boiling it further, all the sulphur will be precipitated as barium sulphate, which can then be readily filtered and washed.

Using an iron crucible does not appreciably increase the figures obtained, as the sulphur taken up from the iron amounts, at the outside, to not

more than $\frac{1}{100}$ to $\frac{2}{100}$ of 1 per cent.   If great accuracy, however, is required, a silver or a nickel crucible can be used.   It is understood of course that all the reagents must be carefully tested for sulphur before they are used in this method.   This is done by running a blank, and the amount of sulphur found should be deducted from that obtained in an analysis.

CHAPTER XVII

TIN

Gravimetric Method. — Treat 1 gram of the finely divided alloy with 15 cc. of strong hydrochloric acid, add a little potassium chlorate from time to time and increase the heat gradually until the alloy is perfectly decomposed. The liquid is boiled to free chlorine, then add from 2 to 3 grams tartaric acid and allow it to dissolve, then dilute to about 400 cc. with hot water. Heat nearly to boiling and pass hydrogen sulphide until the precipitation is complete. Filter and wash with hydrogen sulphide water. If much tin is present the tin sulphide will run through the filter. To prevent this, wash the precipitate with a strong salt solution. Transfer the filter containing the precipitate to a small beaker and digest it with a few cubic centimeters of a colorless solution of potassium or sodium sulphide. Dilute to about 100 cc. and wash with water containing a little sodium or potassium sulphide. The solution contains the sulphides of arsenic, tin and antimony, and the residue on the filter the sulphides of copper, lead, bismuth, etc. Acidulate the filtrate with hydrochloric acid and allow to stand until the arsenic, antimony and tin sulphides mixed with excess of sulphur have settled completely. Filter

and wash with warm water containing sodium chloride, then with alcohol and last with carbon disulphide to dissolve excess of sulphur.   Transfer precipitate and filter to a small beaker and add 5 cc. of strong hydrochloric acid and a little potassium chlorate and warm the mixture.   Add a little more acid or chlorate and heat until the precipitate is dissolved with the exception of a few particles of separated sulphur.   When the sulphides are dissolved dilute with 25 cc. of warm water and add 2 to 3 grams of tartaric acid to keep antimony and tin in solution.   Then add 2 to 3 grams of ammonium chloride and a slight excess of ammonia to the filtrate.   If the solution becomes cloudy on the addition of ammonia, add a little more tartaric acid or ammonium chloride until it clears up.   To the clear solution add 5 cc. of magnesia mixture and one-third the volume of the solution of ammonia.   Cover the beaker and allow to stand in the cold overnight. The arsenic is precipitated as ammonium magnesium arsenate.   Filter and make the filtrate slightly acid with hydrochloric acid.   Now add 20 grams of oxalic acid dissolved in 200 cc. of hot water, dilute to 300 to 400 cc.   Heat nearly to boiling and pass a rapid current of hydrogen sulphide for about half an hour.   The precipitate will contain all the antimony together with a small amount of tin. Filter immediately, as on long standing more stannic sulphide will separate.   Wash with hydrogen sulphide water, and reserve the filtrate.   Dissolve the precipitate in ammonium sulphide.   Pour the ammonium sulphide solution into a boiling

concentrated solution of oxalic acid and pass hydrogen sulphide while the solution continues to boil. Filter and wash with hydrogen sulphide. Drive off excess of hydrogen sulphide with a current of carbonic acid, filter on a porcelain Gooch crucible, wash with water, alcohol, and finally with carbon disulphide to dissolve any free sulphur. Unite the filtrates in a large beaker, add ammonium hydroxide to alkaline reaction, then add ammonium sulphide and acidify with acetic acid. Do not use a stronger acid, as oxalic acid would be set free and hinder the precipitation of stannic sulphide. Filter and wash with a solution of ammonium acetate acidified with acetic acid, which will overcome the tendency of the stannic sulphide to run through the filter. Dry the precipitate and transfer it as completely as possible to a watch glass, burn the filter carefully in a weighed porcelain crucible, moisten the ash with nitric acid, ignite, allow to cool, add the precipitate, cover the crucible, heat gently for some time, remove the cover and heat gently, with excess of air, until all the sulphur is burned off and the stannic sulphide is converted into stannic oxide. Heat over the blast lamp, allow to cool, and heat repeatedly with pieces of ammonium carbonate, to expel the last trace of sulphuric acid. Ignite to constant weight as stannic oxide ($SnO_2 \times 0.78808 = Sn$).

Volumetric Method.[1] — Low's modification of Pearce's method is the best known. It is also very rapid and accurate, taking only about an hour.

[1] Low's " Technical Methods of Ore Analysis," p. 183.

Weigh 1 gram of the finely divided alloy and place
in a thin spun-iron crucible of about 60 cc. capacity,
provided with a loosely fitting porcelain cover.
Add a few drops of water so as just to moisten the
mass (which will prevent subsequent mechanical
loss) and then about 8 grams of stick sodium hy-
droxide. Cover the crucible and heat first very
cautiously until the moisture is expelled, and then
with the full flame of a Bunsen burner until quiet
fusion is attained. Remove the cover and pour
the melt into a clean $2\frac{1}{2}$-inch nickel dish floating
in a beaker of water. Cover the hot cake with a
small porcelain crucible cover, dropped within the
dish, to prevent mechanical loss in case the cake
should crack and fly violently apart.

Place a little cold water in a $5\frac{1}{4}$ inch casserole and
set the hot crucible therein, then turn the latter on
its side so as to admit the water, and heat to boil-
ing. Move the crucible about with a glass rod,
and when the outside is clean wash it off so as to
remove the crucible with the fingers. The inside
of the crucible may still contain some of the undis-
solved melt. Pour in a little water, acidify with
hydrochloric acid, and bring the dilute acid, by
means of a glass rod, in contact with any adhering
melt. When all is dissolved, wash the solution
into the casserole. Now add the detached cake
and the crucible cover with the top (provided with
a loop) up. Cover the casserole and add about
30 cc. of strong hydrochloric acid, which should
prove an ample excess. Heat to boiling, and the
cake will quickly dissolve. It is important not to

have used too much water in washing, etc., as any gelatinous silica dissolves best in strong acid. Now remove and wash off the watch glass covering the casserole and, by means of a bent iron wire, lift out the crucible cover and wash it. Transfer the solution (which should contain no residue of undecomposed alloy) to a 6-ounce flask and add ten $2\frac{1}{2}$-inch iron wire nails or their equivalent. Heat to boiling to produce vigorous action and then set aside for 30 minutes without further heating. All iron and tin salts will be reduced to the ferrous and stannous conditions respectively, and there will be a precipitate of metallic antimony, copper, etc., if these metals are present; also finely divided carbon from the nails. These impurities should be filtered off or they may interfere with subsequent titration. Prepare a moistened plug or filter of absorbent cotton, at least an inch thick, in a funnel, and pour the (still hot) solution through it, retaining the nails in the flask. Wash flask and filter thoroughly with cold water. The absorbent cotton washes very easily. Receive the filtrate in a 12-ounce flask, previously filled with carbon dioxide by adding hydrochloric acid to a little acid sodium carbonate placed in the bottom. Add starch liquor to the filtrate and titrate with standard iodine solution to a blue color. If the liquid is very hot (60° C.) the iodine may act on the ferrous iron and produce an erroneous result, but below 40° C. there appears to be no danger whatever.

Solutions Required. — The iodine solution may be prepared by dissolving 10.6 grams of iodine in a

little water with the addition of about 20 grams of potassium iodide, and diluting to a liter. Standardize as follows: Weigh exactly 0.2 gram of pure arsenious oxide, place in a 6-ounce flask and dissolve in 5 cc. of strong hydrochloric acid, warming very gently but not boiling. Dilute somewhat with cold water, drop in a bit of litmus paper and add powdered sodium carbonate cautiously until the litmus turns blue. Now add 20 cc. of a cold saturated solution of sodium acid carbonate (made from the powdered commercial article), cool if necessary, add a little starch liquor, and titrate to a blue color with the iodine solution. 0.2 gram of arsenious oxide = 0.2404 gram of tin, from which figure the value of the iodine solution may be calculated. The solution does not change materially during a week, but it is not safe to use a standard that is older.

The starch liquor is prepared as follows: Mix 3 grams of starch into a thin paste with cold water and pour into 500 cc. of boiling water. Boil a minute or so and then allow to cool and settle. Pour off the clear liquid into a stock bottle and shake well with about 15 drops of oil of cassia, which will preserve it indefinitely. Mr. Low has observed that copper alone will not precipitate tin under the conditions of the assay, but will easily do so in contact with iron; therefore, if much copper be present in an alloy, the above method of procedure is liable to give a low result. In such a case dissolve 1 gram of the finely divided alloy in a beaker with 6 cc. of strong nitric acid; 3 cc. of water are

slowly added, and the beaker is then quickly covered with a watch glass. When the evolution of brown fumes has ceased, the solution is heated to boiling and diluted with 50 cc. of boiling water. Allow the precipitate to settle completely. Filter off the insoluble residue containing the tin, ignite it in the iron crucible, and then proceed with the assay as usual. In giving this preliminary treatment to material containing tin in a soluble form, it is of course necessary to evaporate the aqua regia mixture to hard dryness and take up again in dilute nitric acid before filtering.

Electrolytic Method. — Dissolve 1 gram of the finely divided alloy in aqua regia, evaporate to dryness, dissolve the residue in 2 or 3 cc. of water, add a concentrated solution of sodium hydroxide containing 2 or 3 grams of sodium hydroxide and then add 80 cc. of sodium sulphide (sp. gr. 1.13 to 1.15). Filter from the sulphides of copper, lead, etc. Dilute to 150 cc., temperature 35°, and electrolyze with a current of $ND_{100} = 1.5$ to 1.6 amperes and 2.1 volts at beginning, 1.45 near the end. Any antimony present will be precipitated in the course of 6 hours on the cathode in the metallic state. The tin and any arsenic present remain in solution, the arsenic being converted into arsenic acid. To separate the tin from the arsenic pour off the solution from the antimony, acidify it with dilute sulphuric acid, heat on the steam bath to remove hydrogen sulphide and filter off the mixture of arsenic and tin sulphides. Dissolve and oxidize the precipitate by heating with hydrochloric acid and

potassium chlorate. Then add ammonia in excess and precipitate the arsenic as magnesium ammonium arsenate with magnesia mixture. Acidify the arsenic-free solution with hydrochloric acid and saturate with hydrogen sulphide gas. Filter off the tin sulphide and dissolve it in ammonium sulphide. Dilute to 150 cc. and electrolyze with a current of $ND_{100} = 1$ to 2 amperes and 3.5 to 4 volts. Temperature 50 to 60°. 0.4 gram of tin will be deposited in an hour's time. When deposition is complete, wash with water and alcohol, dry and weigh as metallic tin. Should any sulphur stick to the end of the cathode it may be removed after washing with alcohol by rubbing with a linen cloth (Classen).

Revolving Cathode or Anode. — By following the following directions 0.5 gram of tin can be deposited in 25 minutes. Current $ND_{100} = 5$ amperes and 7.5 to 10 volts. Speed of anode or cathode 500 revolutions per minute. Volume of solution 100 cc., containing 20 cc. of ammonium sulphide (sp. gr. 0.985).

CHAPTER XVIII

ZINC

Gravimetric Method.—(*Modified Warring Method.*)
Treat 1 gram of the finely divided alloy in a
6-ounce flask with 6 to 10 cc. of strong nitric acid
and heat gently until red fumes have ceased coming
off. If the alloy is not decomposed by this treat-
ment, add 5 cc. of strong hydrochloric acid and heat
for a few minutes. Now add 6 cc. of strong sul-
phuric acid and boil over a free flame until all
traces of nitric acid are expelled and the sulphuric
acid fumes are being freely evolved. Dissolve the
mass in 25 to 40 cc. of water and heat to boiling.
Allow to stand hot for a time until soluble sulphates
are entirely dissolved. Now filter off the lead
sulphate into a 250-cc. beaker. Wash with hot
water and add sufficient sulphuric acid to bring the
free acid in the solution up to 10 or 15 per cent.
The volume of the solution should not exceed 70 cc.
Introduce a piece of heavy sheet aluminum about
an inch square and boil 10 minutes or to complete
reduction. This will precipitate any copper, lead,
cadmium, bismuth, etc., and at the same time reduce
the iron to the ferrous state. Filter and wash
through a filter containing a piece of aluminum into
a beaker containing a stirring rod or strip of the
same metal, cool, add a drop of methyl orange and

neutralize carefully with sodium bicarbonate to a
light straw color.   Add, drop by drop, dilute formic
acid (20 per cent strength) until the pink color is
just restored, then 5 drops more (dilute hydro-
chloric acid, 1 part strong to 6 parts water, may be
substituted for formic acid when ammonium sul-
phocyanate is to be introduced).   Dilute to about
100 cc. for each 0.1 gram zinc possibly present, add,
if much iron is present, 2 to 4 grams ammonium
sulphocyanate, remove the strip of aluminum, heat
nearly to boiling and saturate with hydrogen sul-
phide.   Allow the pure white zinc sulphate to sub-
side for a few minutes, then filter and wash with
hot water.   Transfer precipitate and filter to a
capacious beaker, heat with 8 or 10 cc. of strong
hydrochloric acid and 30 or 40 cc. of water until
the zinc is all in solution.   Cool, and to the cold
solution add 50 cc. or a large excess of sodium
ammonium phosphate (10 per cent solution).   Care-
fully neutralize with ammonia, using litmus as an
indicator, add a drop or two in excess and then
acidify with 1 cc. of acetic acid.   Test and make
sure the solution is acid.   Heat (do not boil, or
bumping will result) for one hour, during which
time the flocculent precipitate will have become
granular and will settle.   Filter through a filter
paper, wash with hot water and dry the paper and
precipitate.   Brush the latter off the former on to a
watch glass, dissolve the small amount of precipi-
tate on the filter in dilute nitric acid into a small
weighed porcelain dish, evaporate to dryness, add
the main portion of the precipitate, and ignite

gently at first and then for a few minutes at a low
red heat. Cool and weigh as zinc pyrophosphate
($Zn_2P_2O_7 \times 0.42914 = Zn$). Considerable time can
be saved by filtering directly into a porcelain Gooch
crucible and igniting as before described.

The flocculent $ZnNH_4PO_4 + H_2O$ is very soluble
in the mineral acids as well as in ammonia, but after
crystallization it is much less soluble in the latter.
It is only slightly soluble in acetic acid; an excess
of 1 cc. in 100 cc. of solution does not dissolve an
appreciable quantity. It is somewhat soluble in
all ammonium salts if only a small excess of phos-
phate is present. The addition of 1 cc. of a 10 per
cent solution of sodium ammonium phosphate for
each 0.005 gram of zinc is sufficient entirely to
prevent its solution in ammonium chloride or sul-
phate, or in the acetate, unless the latter is present
in very large quantity.

Volumetric Method. — Proceed exactly as de-
scribed above until the pure zinc sulphide is dis-
solved by heating in a capacious beaker with 8 or
10 cc. of strong hydrochloric acid and 30 or 40 cc.
of water. Add 3 or 4 grams of pure ammonium
chloride. Dilute to 250 cc. with hot water, heat
to 60° C. and titrate with a standard solution of
potassium ferrocyanide exactly as described in the
following standardization.

Solutions Required. — (1) Standard potassium
ferrocyanide. 21.63 grams of Merck's pure potas-
sium ferrocyanide and 7 grams of sodium sulphite
crystals are dissolved in pure distilled water, the
solution made up to exactly 1 liter and thoroughly

mixed. 1 cc. of this solution should be equivalent to 0.005 gram of zinc.

(2) Uranium acetate (indicator). Dissolve 4.4 grams of the pure salts (Merck's or Schuchardt's) in 100 cc. of distilled water and 2 cc. of acetic acid. This amount is sufficient for 200 zinc determinations. If a pure acetate is not available use the nitrate 52 grams to the liter. The use of ammonium heptamolybdate in 1 per cent solution as an indicator instead of uranium acetate or nitrate is recommended provided all free hydrogen sulphide has been previously expelled from the solution by heating. If a blue color still appears in the test drop, add a crystal or two of sodium sulphite to the zinc solution to decompose any remaining hydrogen sulphide.

Standardization.[1] — Weigh out carefully 0.3 gram of pure zinc (Merck's or Schuchardt's). Metallic zinc for standardizing should be digested with ammonia and ammonium chloride, then washed thoroughly, first with water, then with pure alcohol and well dried. It will then keep for many weeks without sensible change, if not exposed to moisture or acid vapors. If pure zinc is not obtainable, use exactly 0.37338 gram of C.P. freshly ignited zinc oxide (equal to 0.3 gram of zinc) and dissolve in 25 cc. of the dilute hydrochloric acid (1:3), add 3 to 4 grams of pure ammonium chloride and dilute to 200 cc. with distilled water at about 60° C. Titrate at once with the ferrocyanide solution, running in about 58 cc. at once with vigorous stirring. Note

[1] Waring, J. Am. Chem. Soc., XXVI, 18.

the change at this point in the appearance of the
precipitate, a change from bluish-white, thickish
skim milk to nearly pure white, accompanied by a
thinning of the solution and a separation of the
$K_2Zn_3(FeCy_6)_2$ in flocculent form on standing for a
minute, especially if the stirring has been vigorous.
This appearance always occurs at a temperature
of about 60°, when the titration is within 2 or 3 cc.
of completion.   Run in 2 cc. more and the precipi-
tate will lose its flocculent appearance and will
remain suspended for a considerable time.   Test
two or three drops of the solution by running them
off the end of the stirring rod on to a drop of the
indicator placed on a perfectly clean white porce-
lain plate.   The solution must be *thoroughly* stirred
each time and the rod and sides of the precipitating
vessel washed with a jet of hot water, after each
addition of ferrocyanide, before testing.   The test
should give no tinge of brown or even the slightest
flash of discoloration.   Run in the ferrocyanide
now, drop by drop, testing after each addition, until
a distinct, though faint, flash of color is observed.
When a definite reaction is obtained, allow the color
to develop, which will require from two to three
minutes.   Frequently it will be seen that, in addition
to the drop which first gave the reaction, from one
to five of the others develop a brown-red color.
If this be the case, deduct from the burette reading
the fraction of a cubic centimeter corresponding to
the number of drops that show a color in order to
obtain the correct reading.   The dilution coefficient,
i.e. the amount of ferrocyanide necessary to give

a reaction with uranium in a solution of the temperature and volume and containing the amounts of free acid and ammonium chloride that are in the solution being tested, at the end of the titration, is usually about 0.35 cc. and must always be deducted from the burette reading. The standardization should always be made in duplicate or triplicate. To obtain the percentage of zinc in an alloy, multiply the number of cubic centimeters used (less the dilution coefficient) by the percentage value of 1 cc. of the ferrocyanide solution.

NOTES. — The reactions between zinc chloride and potassium ferrocyanide occur as follows: At first the normal zinc ferrocyanide is formed; thus, $4\ ZnCl_2 + 2\ K_4FeCy_6 = 8\ KCl + 2\ Zn_2FeCy_6$ when about 45.5 cc. of the standard ferrocyanide solution has been added to a chloride solution containing 0.3 gram of zinc. If the temperature is low (20° to 25°) it will be found that a yellowish-brown coloration is produced with uranium on the addition of more ferrocyanide. This coloration (which does not appear with hot solution) will, however, fade gradually, but it will be yielded by the solution up to nearly the point at which the precipitate becomes flocculent, when it wholly disappears. The final, and permanent, coloration occurs when the following secondary reaction has been completed, as shown by Konich and Prost:

$$6\ Zn_2FeCy_6 + 2\ K_4FeCy_6 = 4\ K_2Zn_3(FeCy_6)_2.$$

After a little experience the coloration produced after the first reduction causes no difficulty, even with a cool solution, since the color is different and fades on standing instead of becoming more intense, and the solution retains the bluish skim-milk color, which differs from the pure creamy white of the later reaction. The presence of a trace of copper in the solution also affords an indication of the passing of the three-quarter point. The normal ferrocyanide of copper gives a light chocolate tint to the solution if present in the merest trace in a zinc

solution, but when the three-quarter point is passed the chocolate tint changes to a blue, which does not interfere with the final reaction. The presence of copper increases the apparent result by about 1.8 parts zinc for each part of copper.

Electrolytic Method. — Proceed exactly as in the two preceding methods until the pure zinc sulphide is obtained. Filter, wash with hot water. Transfer precipitate and filter to 6-ounce flask and heat with 8 or 10 cc. of strong sulphuric acid and 30 or 40 cc. of water until the zinc is all in solution. Then boil over a free flame until the fumes of sulphuric acid are being evolved freely. Cool, add 25 cc. of water and heat until everything soluble goes into solution. Transfer to a 300 cc. electrolytic beaker. Neutralize[1] with potassium hydroxide and then to the solution add 50 cc. of a solution of potassium oxalate containing 166 grams of the salt to one liter of water and 100 cc. of a solution of potassium sulphate containing 250 grams of the salt to the liter. Total volume should not exceed 250 cc. Electrolyze with a current of $ND_{100} = 0.3$ ampere and 3.9 to 4.2 volts at the ordinary temperature until zinc is removed. To avoid the peculiar spots which electrolytic zinc shows upon a platinum surface, it will be best to first coat the negative electrode with copper (5 grams). In dissolving the precipitated zinc use rather dilute nitric acid. The copper layer will be but slightly attacked, and after washing and drying will serve for further depositions. Wash the zinc deposit with water, alcohol and ether;

[1] Smith's "Electro Analysis," p. 113.

dry in a desiccator.   Oxidation is liable to occur if an air bath be used for the drying.

The zinc may be determined also as follows: To the zinc sulphate solution add 4 cc. of a solution of ammonium acetate, 20 cc. of citric acid, and dilute to 200 cc. with water.   Electrolyze with a current of $ND_{100} = 0.5$ ampere and 4.8 to 5.2 volts at a temperature of 60°.   When the zinc is fully precipitated it can be ascertained by removing a small quantity of the liquid on a porcelain plate and testing with a drop of potassium ferrocyanide. Wash the deposit with water and alcohol.   There is no danger of oxidation during the drying process.

Revolving Cathode or Anode. — To the zinc sulphate solution add 3 grams of sodium acetate and 0.2 cc. of 30 per cent acetic acid and dilute to 125 cc. Electrolyze with a current of $ND_{100} = 4$ amperes and 10 volts.   Speed of anode or cathode 600 revolutions per minute.   Have dish or cathode copper or silver plated.   0.5 gram of zinc can be removed in fifteen minutes.

Kemmerer [1] recommends for the determination of zinc by electrolysis the employment of a cathode of nickel gauze made in the form of a cylinder of such size that it fits loosely in a 150-cc. Jena beaker, and a propeller-shaped anode of platinum.   The latter should be revolved at a speed of about 600 revolutions per minute.   In making the determination itself proceed as described above, method of Warring, until the zinc sulphide is obtained.   Wash this with hot water and dissolve in a little hot dilute

[1] J. Ind. and Eng. Chem., Sept., 1910.

hydrochloric acid, add 2 to 3 cc. of sulphuric acid and evaporate until all of the former and most of the latter acid are expelled. Rinse the zinc sulphate into the 150-cc. Jena beaker and dilute to 100 cc. Add 25 grams of sodium hydroxide and electrolyze, using a current of 6 amperes at a pressure of 4.4 volts. The deposition is complete in fifteen minutes.

To clean the electrode, place it in 2 to 3 per cent sulphuric acid. By this treatment the loss of weight of the cathode can be kept down to 0.5 milligram. When the electrode becomes dark, due to traces of lead, the latter may be removed by pouring a little nitric acid over the electrode.

PART III — SOME APPLIED EXAMPLES
OF ALLOY ANALYSIS

ALUMINUM ALLOY

Containing Aluminum, Manganese and Zinc, with Small Amounts
of Silicon and Iron as Impurities

Silicon. — Weigh into a casserole 1 gram of the alloy and, after covering, pour over it 30 cc. of a mixture of 100 cc. of nitric acid, 300 cc. of hydrochloric acid, 200 cc. of sulphuric acid, and 400 cc. of water. Add the mixture cautiously, a little at a time, if the drillings are fine. When solution is complete, wash down the sides of the casserole and evaporate until copious white fumes are given off. Allow the contents of the casserole to become cool and add 100 cc. of water and a little dilute sulphuric acid. Heat until all soluble salts are in solution and filter, using cone and suction if possible. Wash with water a few times and then remove the filtrate. (Save this for copper.) Wash the precipitate alternately, three times, with boiling hot dilute hydrochloric acid (1:1) and hot water. Finish washing with hot water, five times. Ignite the precipitate in a platinum crucible over a blast lamp and weigh as silica, SiO_2. It may be best to test the purity of this silica by evaporation with a few drops of

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sulphuric acid and a little hydrofluoric acid, in the usual manner, as it may contain alumina.

Copper. — If proper means[1] are at hand, determine the copper in the filtrate electrolytically, after adding a drop or two of nitric acid.

If means for determining copper electrolytically are not at hand, the volumetric method may be used. In case iron is present and aluminum is not to be determined, the copper may be precipitated by aluminum foil as recommended by Low.[2] For this purpose, place several pieces of stout aluminum foil in the Erlenmeyer flask containing the filtrate from the silica.   The pieces of foil should have their corners bent alternately up and down so that they do not lie flat.   Boil the solution 5 or 10 minutes. Shake the flask a little to loosen the copper from the foil and add to the solution 15 cc. of strong hydrogen sulphide water.   Allow to settle a moment and filter.   Drain the flask the last time.   Now pour through the paper into the flask 10 cc. of warm dilute nitric acid (1:1).   Remove the aluminum when all the copper is dissolved and rinse off with water. Pour 5 cc. of bromine water through the filter. Wash the filter also a few times with hot water. Boil off the excess of bromine from the filtrate and add a slight excess of strong ammonia.   Boil off this excess also and acidify with acetic acid, dissolving any precipitate which may form by boiling and adding a little more acetic acid.   Cool, add

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[1] See Chapter II.

[2] "Methods of Ore Analysis," p. 80.

3 grams of potassium iodide and titrate at once with the thiosulphate.

Aluminum. — Determine the aluminum in the filtrate from the copper. If hydrogen sulphide has been used to precipitate the copper, boil off the excess of this and add a few drops of nitric acid and again boil. Separate the aluminum from the zinc and manganese by a double basic acetate separation. The manganese may then be determined in the filtrate from the aluminum by the use of hydrogen sulphide. This method of procedure is, however, long and tedious, and for most purposes the simplest way of determining zinc and manganese is in separate samples and the aluminum by difference will prove much more satisfactory.

Manganese. — Dissolve 1 gram of the alloy in 30 cc. of dilute hydrochloric acid, then add 25 cc. of concentrated nitric acid and evaporate to 10 cc. Add 50 cc. of colorless nitric acid and boil. Now precipitate the manganese with potassium chlorate and determine as is usual in the Williams method for manganese in iron and steel.

Zinc. — Evaporate the filtrate from the manganese to dryness but do not bake. Cool and add 7 grams of ammonium chloride, 25 cc. of hot water and 15 cc. of strong ammonia. Boil and rub the dish with a rubber-tipped rod to break up the lumps, etc. Filter and wash several times with boiling water containing 10 grams of ammonium chloride to the liter. Now add 25 cc. of concentrated hydrochloric acid and 40 grams of test lead. Stir until the liquid is colorless and then a minute longer.

Titrate with ferrocyanide solution in the usual manner.

The following modification of the above scheme may also be used.

Copper and Manganese. — In the filtrate from the silicon determine the copper and manganese simultaneously as follows: Add a drop or two of nitric acid to the filtrate. Dilute to 150 cc. Electrolyze with a current of $ND_{100} = 0.5$ ampere and 2.5 volts. The manganese will be deposited upon the anode as dioxide and the copper will be deposited at the same time on the cathode. The electrodes used by the authors consist of two cylinders, one fitting inside the other. Wash the manganese dioxide on the anode with water and alcohol, dry and ignite. The dioxide will be converted into Mn_3O_4. $Mn_3O_4 \times 0.72026 = Mn$. Wash the copper on the cathode with water and alcohol, dry, cool and weigh. The increase in weight is metallic copper.

Aluminum. — Determine the aluminum in the filtrate volumetrically as described in chapter on Aluminum, p. 42.

Zinc. — The zinc must then be determined in a separate sample as $Zn_2P_2O_7$ or by Warring's modified method as described in chapter on Zinc, p. 139.

Iron. — Determine iron in a separate sample by titration with potassium permanganate as described in chapter on Iron, p. 78.

Alloy of Antimony and Arsenic

The simplest and most accurate method of separating the two metals is by electrolysis, while the volumetric is the most rapid. A full description of the gravimetric, volumetric and electrolytic methods of determining and separating the two metals will be found in the chapters on Antimony and Arsenic, pp. 45 and 51. Treat 1 gram of the alloy, as there directed.

Alloy of Antimony, Arsenic and Tin

The gravimetric, volumetric and electrolytic separation and determination of the three metals have already been described in chapters on Antimony, Arsenic and Tin, pp. 45, 52 and 131.

The volumetric method of separating the antimony and arsenic is the most rapid. Determine the tin volumetrically in a separate sample as described in chapter on Tin, p. 133. Tin may also be determined in the same sample by the method of W. H. Low,[1] after the determination of antimony by titration with permanganate. The titrated solution contains antimonic chloride and stannic chloride besides other things of no particular moment. Pour this solution into a 500-cc. round-bottom flask and rinse out the flask or beaker in which the antimony was titrated with about 50 cc. of strong hydrochloric acid and add washings to the main solution. The main solution should be at least one-fifth by volume of strong hydrochloric acid. Add about 1 gram of finely powdered C. P. antimony and place on the steam bath for about 15

[1] J. A. C. S., Vol. XXIX, 1907, p. 70.

minutes, shaking once in a while. Next remove from the bath and connect with an apparatus capable of giving a rapid current of carbon dioxide. The connection is made by means of a cork carrying two tubes. The first dips below the surface of the solution in the flask and the second or outlet tube is bent downward and the end dips slightly below the surface of some water or mercury. This allows any tendency to back pressure to be instantly detected. While passing a rapid stream of gas heat the contents of the flask to boiling, using a naked flame, but taking care to heat the sides of the flask and avoid directly heating the bottom. This is because the antimony lies on the bottom and the flask might be cracked by unequal heating in contact with solution. Boil from 2 to 3 minutes after the liquid commences to boil. Cool quickly by surrounding the flask with cold water, and take care that the current of carbon dioxide is strong enough to prevent back pressure due to sudden condensation. When cold, loosen the cork somewhat and introduce 5 cc. of good starch solution, and then withdraw the flask gently so as not to allow air to enter by forming currents. Cork quickly and take to the burette. Introduce the spit of the burette far down into the neck of the flask and, rotating the latter gently, run in a drop of N/10 iodine solution (same as used in chapter on Tin, p. 135). Towards the end the starch blue will appear and remain mostly in the middle portion of the solution, requiring stronger agitation to mix with the rest of the solution. This causes the metallic antimony in

the bottom of the flask to become stirred up and slightly obscure any slight blue tint. For this reason the titration is continued till the last drop gives a strong blue to the whole solution, and then we deduct about 0.05 cc. from the burette reading. Lead in large amount does not interfere. Theoretically any amount of copper should not interfere.

Alloy of Antimony and Tin

Gravimetric Method. — The two metals are separated by means of oxalic acid as directed in chapter on Tin, p. 131, and the antimony determined as directed in chapter on Antimony, p. 45, as Sb_2S_3 or Sb_2O_4 and then tin as SnO_2 as described in chapter on Tin, p. 131.

Volumetric Method. — Treat 1 gram of the finely divided alloy in a 6-ounce flask with 7 grams of potassium acid sulphate, 1 gram of tartaric acid and 10 cc. of strong sulphuric acid. Heat over a free flame (manipulating the flask in a holder), cautiously at first, until the alloy is thoroughly decomposed and all separated sulphur has been boiled out of the flask and the separated carbon is completely oxidized, leaving a clean mass with but little free sulphuric acid. Allow to cool with the flask on its side, as otherwise the solidifying cake may break it. Cool, add 50 cc. of water and 10 cc. of strong hydrochloric acid. Heat to effect solution and then boil for a few minutes to expel any possible sulphur dioxide. Finally add 10 cc. more of strong hydrochloric acid. Cool under the tap. Dilute to about 200 cc. with cold water and titrate with

the standard solution of permanganate described under Iron, p. 78. The iron value multiplied by 1.0751 will give the antimony value. Now determine the tin in the same solution by titrating with N/10 iodine as described under Alloy of Antimony, Arsenic and Tin. Tin may also be determined in separate sample volumetrically, as directed in chapter on Tin, p. 133.

Electrolytic Method. — Treat 1 gram of the finely divided alloy as directed in chapter on Antimony, p. 45. As tin cannot be reduced from a sodium sulphide solution, the sodium sulphide solution free from antimony must be converted into ammonium sulphide. Classen proceeds as follows: Treat the antimony-free solution with about 25 grams pure ammonium sulphate free from iron, and heated very carefully with the dish covered, till the hydrogen sulphide has all escaped; the solution is then kept in gentle ebullition for about fifteen minutes. Complete conversion into ammonium sulphide is shown by the greenish-yellow color of the solution. If the heating is continued too long, tin sulphide may separate; it can be dissolved in ammonium sulphide. After it is completely cooled, any sodium sulphate that may have separated is dissolved by addition of water, and the solution electrolyzed as directed in chapter on Tin, p. 137.

Alloy of Antimony and Lead

The following method devised and used by Price is a modification of Neuman's method for the separation of lead and antimony, combined

with the titration of antimony in the *ous* condition with potassium permanganate. It is very accurate and rapid, both metals being determined in an hour's time. Treat 1 gram of the finely divided alloy in a covered evaporating dish with from 1 to 5 grams of tartaric acid (depending on the amount of antimony present), 15 cc. of water and 4 cc. strong nitric acid and heat on the steam bath until the alloy is dissolved. To the clear solution add very cautiously, with constant stirring, 4 cc. of strong sulphuric acid. Dilute with 50 cc. of distilled water and allow to cool. All the lead will be precipitated as lead sulphate. Filter through a platinum Gooch crucible. Wash the lead sulphate and ignite as directed in chapter on Lead, p. 87. The filtrate contains all the antimony free from lead. Add 10 cc. of strong sulphuric acid and 4 grams of potassium acid sulphate to the solution, transfer it to a 6-ounce flask and boil over a free flame until nitric acid is completely expelled and all organic matter has been destroyed. From this point proceed exactly as described for determination of antimony by titration with permanganate in Alloy of Antimony and Tin, p. 154. This method can be made more rapid by determining the antimony in a separate sample as directed in Alloy of Antimony and Tin, p. 154.

Electrolytic Method.— Proceed exactly as directed above until lead sulphate is obtained on the filter and antimony in the filtrate. Dissolve the lead sulphate in 15 cc. of strong nitric acid. Dilute to 150 cc. and electrolyze as directed under Lead, p. 92.

Make the filtrate strongly alkaline with sodium hydroxide. Then add 50 cc. of saturated sodium sulphide solution, heat to boiling. Filter from any black residue (sometimes lead and antimony alloys, such as type metal, contain a little copper, which will be precipitated as copper sulphide). Electrolyze the still warm solution as directed under Antimony, p. 50. If any copper is present dissolve the black residue in 8 cc. of dilute nitric acid (1:1), add 1 cc. sulphuric acid and electrolyze as directed under Copper, p. 71, or evaporate to fumes and determine copper volumetrically as directed in Copper, p. 66.

SCHEME A [1]

BABBITT METAL

Alloy of Sn, Cu, Sb, Pb and Zn

(a) **Tin.** — Weigh 1 gram of the alloy in fine drillings into a small beaker or dish and add 20 cc. of dilute nitric acid (sp. gr. 1.15). Cover with a watch glass and when action ceases remove this and evaporate to dryness on a water bath. Bake for one hour in an air bath at 120° C., cool, moisten with 3 to 4 cc. of nitric acid, dilute to about 30 cc., digest and filter on a small paper. Wash until the washings cease to react acid. Dry the precipitate and separate from the paper. Ignite the latter in a weighed porcelain crucible, moisten the ash with a drop or two of nitric acid and ignite gently. Add the precipitate to the ash in the crucible and ignite

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[1] Meade, Chemical Engineer, VIII, 45.

at a red heat.   Weigh as $Sb_2O_4 + SnO_2$.   Determine the antimony as described in (a) or (b), calculate to Sb_2O_4 and subtract from the above weight for SnO_2. $SnO_2 \times 0.7881 = Sn$.

(b)[1] **Antimony.** — Weigh out a fresh sample of **1** gram.   Boil this in a small beaker with 1 gram of potassium iodide, 40 cc. of water and 40 cc. of concentrated hydrochloric acid, for one hour.   Allow the deposited antimony to settle and decant off the liquid through a small filter paper.   Wash the antimony by decantation six or seven times with hot dilute (1:5) hydrochloric acid.   This can be easily and thoroughly done, since it is very heavy and settles completely.   Pour the washings through the paper and wash the latter with hot dilute hydrochloric acid until the paper is free from lead chloride.   Place the paper containing a small trace of antimony in a large weighed porcelain crucible, moisten with nitric acid and ignite gently.   During the ignition cover the beaker containing the antimony with a watch glass and add a little (3 or 4 cc.) of strong nitric acid and heat.   This converts the antimony to an oxide.   When the filter paper is burned, cool the crucible and transfer the precipitate from the beaker to this, using a little water if necessary.   Evaporate the contents of the crucible to dryness and ignite.   Weigh as Sb_2O_4. $Sb_2O_4 \times 0.7898 = Sb$.

(c)[2] **Volumetric Method.** — Boil 1 gram of drillings with 1 gram of potassium iodide, 40 cc. of water and

[1] Andrews, J. Am. Chem. Soc., XVII, 869.

[2] Yockey, J. Am. Chem. Soc., XXVIII, 646 and 1435.

40 cc. of concentrated hydrochloric acid for one hour. Filter on asbestos and wash five times with dilute (1:10) hydrochloric acid. Wash precipitate and asbestos into a beaker and add 20 cc. of concentrated hydrochloric acid and a few crystals of potassium chlorate. Warm and stir until all the precipitate goes into solution. Then dilute to 100 cc. and filter the asbestos out, washing with water until the washings are no longer acid. Boil until free chlorine is expelled, which requires about five minutes. Cool to room temperature, add 1 gram of potassium iodide and titrate the liberated iodine with standard thiosulphate.

(d) **Lead.** — To the filtrate from the antimony and tin add 10 cc. of dilute (1:1) sulphuric acid and evaporate until copious white fumes are given off. Cool, dilute, warm and filter. Wash with 2 per cent sulphuric acid. Remove the filtrate from under the funnel and wash the precipitate with alcohol until the washings no longer react acid. Dry the residue, separate the paper and precipitate, burn the former in a weighed porcelain crucible, moisten the ash with a few drops of nitric acid and heat. Add a drop of sulphuric acid, drive off the acid on the hot plate and ignite gently. Add the rest of the precipitate to the contents of the crucible, ignite and weigh as $PbSO_4$. $PbSO_4 \times 0.6831 = Pb$.

(e) **Volumetric Method.** — To the filtrate from the antimony and tin add 10 cc. of dilute (1:1) sulphuric acid and evaporate until copious white fumes are given off, cool, dilute, warm and filter. Wash three or four times with 2 per cent sulphuric acid and

then once with cold water.   Dissolve the lead sulphate that is on the paper by pouring through it 10 grams of ammonium acetate dissolved in 50 cc. of hot water.   Allow the solution to run into the beaker containing the main body of the precipitate. Wash the paper a few times with hot water.   Heat the contents of the beaker until the lead sulphate dissolves, dilute to 20 cc., make barely acid with acetic acid and titrate with standard ammonium molybdate solution until a drop of the solution placed upon a drop of tannic acid solution gives a yellow color.   The standard ammonium molybdate solution is made by dissolving 8.64 grams of the salt in a liter of water.   Standardize against pure lead foil by dissolving in nitric acid, evaporating with sulphuric acid, etc., as above.   The tannic acid indicator is prepared by dissolving 0.1 gram of tannic acid in 30 cc. of water.

(*f*) **Copper.** — The filtrate from the lead is heated to boiling and hydrogen sulphide is passed through it until it becomes cold.   The precipitate settles quickly, in large flocks, and may be readily filtered off.   (Before filtering, however, hydrogen sulphide is passed through the water to be used in washing until the latter smells of it.)   Filter, using suction if obtainable.   Collect the precipitate into the point of the funnel and then wash thoroughly, keeping the precipitate always covered with a hydrogen sulphide wash water.   Ignite wet over a low flame in an inclined porcelain crucible and after the paper is burned increase the heat, finally using the blast lamp. Cool and weigh as CuO.   CuO × 0.7989 = Cu.

(g) **Volumetric Method.**— To the filtrate from the lead sulphate add ammonia until the solution is faintly alkaline and then 8 cc. of acetic acid and 3 grams potassium iodide. Titrate the liberated iodine with standard thiosulphate solution after adding a few cubic centimeters of starch indicator, until the blue color disappears. If zinc is present in the babbitt, the copper should be precipitated with hydrogen sulphide as described in (e). Copper sulphide is easily filtered and washed. It should be dissolved in a few cubic centimeters of nitric acid and all except 2 or 3 cc. of the latter expelled by evaporation. The ammonia and acetic acid are then added, etc. The thiosulphate is standardized against copper foil by dissolving 0.1 gram in 5 cc. of nitric acid, evaporating to 3 cc. and adding 6 cc. of ammonia, then 8 cc. of acetic acid, etc.

(h) **Electrolytic Method.**— Place the filtrate from the lead sulphate in a weighed platinum dish and connect the latter with the − or zinc pole of an electric battery. Insert into the solution a platinum wire connected with the + or copper terminal. The two should not touch. In place of a set of batteries the electric light current may be used provided its strength is reduced. A convenient way of doing this is to pass the current through six 16-c.p. lamps in series. The copper is deposited upon the cathode at once and bubbles begin to come off the anode. Should the copper begin to be deposited upon the rod and the bubbles on the sides of the dish, the apparatus is connected up wrong. In this event exchange terminals, when

the copper will come off the rod and be deposited upon the dish.   Should the deposit of copper appear mossy in form, the current is too strong.   After seven or eight hours, or in the morning if the solution has been left overnight, the deposition of the copper will be complete.   When all trace of blue color has left the solution, tilt the dish a little so as to expose a fresh platinum surface, and allow the current to pass through the solution for half an hour longer.   If at the end of half an hour no copper appears on the clean platinum surface, the deposition may be considered complete.   Siphon off the liquid from the dish without interrupting the current, running cold water from a wash bottle around the sides of the dish at the same time. Interrupt the current and wash the deposit first with water and then once with strong alcohol. Dry the dish in the air bath or by lighting the alcohol, cool and weigh.   The increased weight is metallic copper.

(*i*) **Zinc.** — To the cold filtrate from the copper add 50 cc. of sodium ammonium hydrogen phosphate (10 per cent solution).   Carefully neutralize with ammonia, using litmus as an indicator, add a drop or two in excess and then acidify with 1 cc. of acetic acid.   Test and make sure the solution is acid.   Heat (do not boil, or bumping will result) for one hour, during which time the precipitate will become granular and settle.   Filter through a filter paper, wash with hot water and dry the paper and precipitate.   Brush the latter off the former on to a watch glass, dissolve the small amount of pre-

cipitate on the filter in dilute nitric acid into a small weighed porcelain dish, evaporate to dryness, add the main portion of the precipitate, and ignite gently at first and then for a few minutes at a low red heat. Cool and weigh as $Zn_2P_2O_7$. $Zn_2P_2O_7 \times 0.4291 = Zn$.

(*j*) **Volumetric Method.** — Heat the solution to boiling and titrate with standard ferrocyanide solution until a drop of the liquid mixed with a drop of a strong solution of uranium nitrate on a white plate shows a brown tinge after standing a few minutes. To save time make a number of tests 0.1 cc. apart and take the reading on the burette corresponding to the one developing in 3 minutes. The standard ferrocyanide solution should contain 44 grams of potassium ferrocyanide per liter, and may be standardized against either pure zinc or pure zinc oxide (= 80.34 per cent zinc) dissolved in dilute sulphuric acid.

NOTE. — The above scheme while a very simple and convenient one for finding out the approximate composition of an alloy is not a very accurate one. All the iron in the alloy and some of the lead and copper remain in the insoluble matter from the nitric acid solution, while some of the antimony is unoxidized and passes into the filtrate with the copper, lead and zinc. The accuracy of the scheme can be much increased by the following procedure. The precipitated and weighed $SnO_2 + Sb_2O_4$ are fused with six times their own weight of a mixture of dry sodium carbonate and sulphur (or sodium thiosulphate alone). The fusion should be carried out over a low flame in a porcelain crucible and continued until no odor of sulphur dioxide is perceptible and no blue flame of burning sulphur is observed between the crucible and its cover. When cold the fusion is dissolved in hot water, tin, antimony and some copper and iron going into solution,

forming a deep-brown solution. Sodium sulphite is now added to the solution until it changes to slightly yellow in color, which precipitates any copper and iron as sulphides. Tin and antimony remain in solution as sodium sulphostannate and sulphoantimonate respectively. The iron and copper sulphides are filtered off, washed well with water containing hydrogen sulphide, ignited and weighed as CuO and Fe_2O_3. This weight is subtracted from the weight of impure Sb_2O_4 and SnO_2 obtained. The copper and iron oxides are then dissolved in a little strong hydrochloric acid. The solution is diluted to 20 or 25 cc., made strongly ammoniacal, filtered and washed. The precipitate is ignited and weighed as Fe_2O_3, from which the iron is calculated. The filtrate is acidified with dilute H_2SO_4 and added to the main solution for the copper.

To determine the antimony in the filtrate from the $Sb_2O_4 + SnO_2$ make the filtrate from this insoluble residue nearly alkaline with caustic soda and add 15 to 20 cc. of yellow ammonium sulphide solution. Filter and wash. Precipitate contains all the copper, lead and zinc. Acidify the filtrate with dilute sulphuric acid and filter off the small amount of antimony precipitated on a small weighed filter paper. Wash with water. Dry, wash free from sulphur with carbon bisulphide and then with ether. Dry at 100° C. and weigh as Sb_2S_3. Calculate to Sb_2O_4 and add to the combined weights of Sb_2O_4 and SnO_2.

Dissolve the precipitate of copper, lead and zinc sulphides in nitric acid and determine lead, copper and zinc as described in the above scheme, in (c), (d), (e), (f), (g) and (h).

SCHEME B

The scheme outlined below will give very accurate results but is very troublesome.

Weigh 1 gram into a 6-ounce beaker, cover and dissolve in 10 cc. of aqua regia. Add a little potassium chlorate and heat. Add a little tartaric acid and dilute with water. Make alkaline with

sodium hydroxide and add 15 to 20 cc. of sodium sulphide solution (made by dissolving 75 grams of sodium hydroxide in 100 cc. of water and saturating with hydrogen sulphide). Heat the liquid, stirring frequently, for 30 to 45 minutes. Allow the precipitate (sulphides of copper, lead, zinc and iron) to settle, filter through a small filter paper and wash well with hot water containing 2 per cent of the above sodium sulphide solution. Treat the precipitate as directed for lead below and the filtrate as directed for antimony and tin.

(k) **Antimony.**[1] — Make the filtrate up to a volume of 500 cc. in a graduated flask and measure 250 cc. (= 0.5 gram alloy) of this into an 18-ounce beaker. Dilute to 300 cc. and add cautiously 30 grams of oxalic acid in the form of crystals. Heat on the hot plate until everything is in solution except possibly a few flakes of orange Sb_2S_3. Boil ten minutes and pass a rapid current of hydrogen sulphide through the solution for 20 minutes. Antimony is precipitated, usually contaminated by a little tin. Allow to stand in a warm place until the odor of hydrogen sulphide has nearly gone from the solution, filter through a small filter and wash a few times with hot water. Now wash the precipitate back into the beaker in which it was made, place this beaker under the funnel and dissolve the small amount of antimony sulphide adhering on the filter by pouring a few drops of very dilute sodium hydroxide through it and wash. Add 15 cc.

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[1] Clark's method. See also Treadwell-Hall, "Analytical Chemistry," Vol. II, 188.

of sodium hydroxide solution (10 per cent) to the contents of the beaker and warm until all antimony is in solution. Add 20 grams of oxalic acid, heat to boiling and pass hydrogen sulphide through the solution as before. Allow the solution to stand in a warm place until the odor of hydrogen sulphide is faint.

Filter the antimony sulphide on a small paper and wash with hot water. Wash the precipitate back into the beaker and dissolve in sodium sulphide (of 1.13 to 1.15 sp. gr.), pouring a little on the paper to dissolve the adhering precipitate and washing the former until free from alkaline sulphide, catching the washings in the beaker with the main solution of the precipitate. Pour the sodium sulphide (solution should measure 125 cc.) into a large weighed platinum dish, add 2 grams of potassium cyanide, heat to 60 to 65° C. and deposit the copper with a current of $ND_{100} = 1$ ampere and 1.1 to 1.7 volts. To ascertain when all the metal has been deposited, incline the dish slightly, thus exposing a clean platinum surface. If it remains bright for half an hour the precipitation is finished. Wash the deposit with water without interrupting the current. Then disconnect, rinse the dish well with water, then with alcohol, dry at 90° C. and weigh; increase in weight is antimony.

(*l*) **Tin.**[1] — The combined filtrates from the two antimony precipitations are evaporated with 30 cc. of strong sulphuric acid until dense white fumes of sulphuric anhydride appear. This can be done

[1] Wilson's method. Chem. Eng., II, 144.

most rapidly in a large evaporating dish. Cool, dilute cautiously to 300 cc. and filter. Warm the filtrate to 70° C. and pass hydrogen sulphide through it for 20 minutes. Filter off the stannous sulphide, dry, ignite in a porcelain crucible and weigh as SnO_2. $SnO_2 \times 0.7881 = Sn$.

Lead. — The residue containing sulphides of lead, copper, iron and zinc is roasted in a porcelain dish to change the sulphides to sulphates, etc., and to get rid of the filter paper. After cooling, dissolve the residues in nitric acid, and when action ceases add 10 cc. of dilute (1:5) sulphuric acid and evaporate until dense white fumes come off. Cool, dilute, filter, wash and ignite the lead sulphate as directed above in (d).

Copper. — The copper is determined in the filtrate from the lead sulphate as directed in (h) and the filtrate or the solution in the dish is saved for iron and zinc.

Iron. — Heat the filtrate from the copper to boiling, and if the latter was precipitated by hydrogen sulphide, expel this gas by boiling. Add a few drops of nitric acid or a few cubic centimeters of bromine water and boil for a few minutes. Add ammonia in excess, boil and filter. Wash a few times with water, set the filtrate to one side and redissolve the precipitate of iron in dilute nitric acid, allowing the solution to run into the beaker in which the precipitate was formed. Wash the paper free from iron with water. Heat the solution to boiling and reprecipitate the iron with ammonia. Boil a minute, and filter into the filtrate from the

first precipitation. Wash a few times, ignite and weigh as Fe_2O_3. $Fe_2O_3 \times 0.7 = Fe$.

Zinc. — Determine in the filtrate from the iron as directed in (*i*).

SCHEME C

The following is the method employed by Mr. William B. Price for the analysis of Babbitt metal containing tin, lead, antimony and copper.

BABBITT METAL

Tin, Antimony and Copper are the metals in genuine Babbitt. Cheap Babbitt consists of tin, lead, antimony and copper. In either case the method of analysis is along the same lines. To analyze a sample containing all four metals, determine the tin and antimony volumetrically or electrolytically as directed under Alloy of Tin and Antimony, p. 154. In a separate sample determine the lead and copper as follows: Treat 1 gram of the finely divided alloy in a 250-cc. covered beaker with 10 cc. of aqua regia. Add a little potassium chlorate and heat. Add a little tartaric acid and dilute with water. Make slightly alkaline with sodium hydroxide, and add 15 to 20 cc. of saturated sodium sulphide solution. Digest on the steam bath for a half hour, stirring frequently. Allow the precipitate of lead and copper sulphide to settle. Filter and wash with a 2 per cent solution of sodium sulphide. Dissolve the sulphides of copper and lead in 15 cc. of strong nitric acid. Dilute to 150 cc. and determine the lead and copper electrolyti-

cally at the same time. Two cylinders are used, one fitting inside the other. Electrolyze with a current of $ND_{100} = 1.5$ amperes and 1.4 volts. The lead will all be precipitated in the course of an hour upon the anode, and the copper will be deposited at the same time on the cathode. The lead separates first and the copper more slowly. When the lead is fully precipitated wash with water and alcohol and dry for 15 minutes at a temperature from 200° to 230° C. Cool and weigh. $PbO_2 \times 0.8643 = Pb$.

Copper. — Neutralize the solution with ammonia, add 4 cc. of nitric acid (sp. gr. 1.42) and 1 cc. sulphuric acid (sp. gr. 1.84) and electrolyze with a current of $ND_{100} = 0.5$ ampere and 2 volts, until copper is fully precipitated. Wash with water and alcohol, dry, cool and weigh. Increased weight is metallic copper. Or add 8 cc. of strong sulphuric acid to the nitric acid solution of the sulphides. Evaporate to fumes and determine lead as sulphate as directed under Lead, p. 87, and the copper in the filtrate volumetrically as directed under Copper, p. 66.

SCHEME D

Mr. D. J. Demorest[1] suggests the following excellent method for the determination of tin and antimony in Babbitt metals, etc. It depends upon the fact that the oxides of antimony and tin may be separated from copper and lead by double precipitation with sodium sulphide in a strongly alkaline solution. His method follows.

[1] J. Ind. and Eng. Chem., March, 1910.

Tin and Antimony. — One gram of the alloy is placed in a 200-cc. beaker and covered with 20 cc. of water. In this are dissolved 5 grams of tartaric acid and then 10 cc. HNO_3 (sp. gr. 1.42) are added. This will dissolve the alloy quickly unless it is in large pieces, which it never need be. When dissolved the solution is diluted to 50 cc. and a strong solution of NaOH is poured in until the hydroxides first formed dissolve and leave the solution clear. The liquid should not be heated, as this may cause a precipitate of metastannic acid to commence to form in the alkaline solution. The solution is poured slowly and with constant shaking into a flask containing 150 cc. of a boiling hot solution of 10 grams of NaOH and 10 cc. of a colorless saturated solution of Na_2S. (The solution should be colorless or some copper will remain in the solution.) The contents of the flask are agitated for several minutes and then allowed to settle. The sulphides of lead and copper will settle quickly and compactly. · The clear solution is decanted as closely as possible through a strong filter paper folded in ribs. The precipitate is washed twice by decantation, using about 25 cc. of water each time.

" Now to the sulphides in the flask 5 cc. of HNO_3 are added and heated until the black sulphides disappear. Then the solution is made alkaline with NaOH again and 10 cc. Na_2S solution added and heated and shaken vigorously for several minutes. Again the supernatant liquid is decanted through the same filter, washed twice by decantation and

then the sulphides transferred to the filter and washed twice more with hot water containing a little Na_2S. The filter paper with its contents is placed in a crucible and heated gently so as to dry the sulphides. While these are drying, sulphuric acid is added under a hood to the filtrate which contains the Sb and Sn until the solution, which should have a volume of from 400 to 500 cc., is acid. The liquid is stirred well and allowed to settle for a few minutes, then decanted through a filter paper as closely as possible to get rid of the greater part of the liquid. The beaker containing the sulphides of antimony and tin is set under the funnel, and 25 cc. of the NH_4HS solution diluted to 50 cc. are poured through. This will dissolve the sulphides. The solution is transferred to a 300-cc. beaker, diluted to 150 cc., 4 to 5 grams KCN are added, and the solution electrolyzed, the solution being rapidly rotated."

The cathode used by Demorest was a cylinder of platinum gauze, 2 inches high and 1 inch in diameter. He used a stationary anode, but kept the solution stirred by means of a platinum paddle operated by a water motor. The voltage used was 8 to 10 volts and the current 5 to 6 amperes. This large current will heat the solution considerably and it is best to set the beaker in a basin of water. The KCN keeps sulphur from separating out on the anode in excess by forming KCNS with the polysulphides.

The tin and antimony should be deposited in 30 to 60 minutes, depending on the amounts present.

The cathode is lifted out and washed first with water, then with alcohol, and dried on a steam plate. If any pieces of sulphur are entangled in the meshes of the gauze, dip the cathode in CS_2 before washing with alcohol.   This, however, is rarely necessary.

After weighing, the solution is again electrolyzed for ten minutes and the cathode washed and weighed. If the weight has not increased more than 1 mm. in these ten minutes the electrolysis is complete. The weight represents the antimony and tin.

Antimony. — After the cathode is weighed it is placed in a small beaker and 5 cc. of strong HNO_3 are poured over it from a pipette. The acid is heated and the beaker tipped and the electrode turned so that the HNO_3 will dissolve off all the deposit that is possible.   There will always be some black stains left on the cathode, which are very difficult to remove with HNO_3. The gauze is washed with a fine jet of water over the beaker. Then the gauze is set into another small beaker and 60 cc. of strong HCl are poured over it, which will dissolve off the black stains.   The HNO_3 is used first to avoid the loss of antimony as SbH_3, which would take place if the deposit were dissolved in HCl alone.

The gauze is then washed into the HCl with a jet of water and the two solutions poured into a 500-cc. Erlenmeyer flask and the beakers washed with a little more HCl.   The solution should be boiled vigorously for 10 to 15 minutes to decompose the HNO_3.

Or, instead of mixing the two solutions, the 5 cc. of HNO_3 are evaporated to dryness in a platinum dish (for speed), then the residue is dissolved in 60 cc. HCl.   This last way is the better, but takes more time.

Now to the hot HCl solution 5 grams of $KClO_3$ are added in small amounts at a time, then 50 cc. H_2O are poured in and the solution boiled while passing through a stream of CO_2 until the free chlorine is all gone, as shown by starch-iodine paper. This takes 15 to 20 minutes.

The $KClO_3$ must not be added before the HNO_3 is decomposed, for the KNO_3 formed greatly prolongs the time necessary to get rid of all free chlorine.

When the free chlorine is all gone water is added to make a volume of 150 cc. and the solution cooled under tap water while passing in a stream of CO_2 to displace the air.   The solution should be colorless. The CO_2 is made from marble and HCl.

When cool, the current of CO_2 is stopped, 4 grams KI are added and the liquid stirred until the KI is all dissolved.   Then standard $Na_2S_2O_3$ solution is run in until the color due to iodine all disappears, starch solution is added, and the excess "thio" titrated back with standard $K_2Cr_2O_7$ until a blue color is obtained.   This should take only a few drops.   The authors prefer this end point to merely titrating with $Na_2S_2O_3$ until the blue starch iodide disappears.

The $KClO_3$ oxidizes the antimony to H_3SbO_4. This liberates iodine in the reaction:

$$H_3SbO_4 + 2\ KI + 2\ HCl = 2\ KCl + H_3SbO_3$$
$$+ 2\ I + H_2O.$$
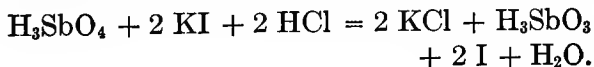
Then the thiosulphate is oxidized by the iodine in the reaction: $2 Na_2S_2O_3 + 2 I = Na_2S_4O_6 + 2 NaI$.

Demorest standardized the thiosulphate against $K_2Cr_2O_7$ of known iron strength and also by treating Sb_2O_5 or Sb or tartar emetic by dissolving them in HCl and $KClO_3$ and treating as above. The two methods of standardization check very closely. The iron strength of the bichromate, multiplied by 1.0751, gives its antimony value. The " thio " solution is made by dissolving 20.7 grams of $Na_2S_2O_3 5 H_2O$ and diluting to one liter.

There is nothing which can be deposited with the antimony and tin which will interfere with the process. Arsenic does not interfere.

Copper and Lead. — While the electrolysis of the antimony and tin is going on, the dried sulphides of lead and copper are crumpled into a beaker, the paper burned and the ash added to the rest of the precipitate in the beaker. The sulphides and ash are dissolved in 40 cc. concentrated HNO_3. In this solution the lead may be determined as sulphate and the copper in the filtrate from the lead titrated by the iodide method. But it is much quicker and more accurate to determine the two electrolytically, according to the following:

The solution is diluted to 100 cc., 50 cc. are pipetted into a platinum dish, 50 cc. of water added and electrolyzed with a potential of six volts for a few minutes. The voltage is then increased to 10 to 12 volts, keeping the solution stirred. The lead is all deposited on the dish, which is the anode, in about 15 minutes. Then part of the HNO_3 is

neutralized with ammonia and the electrolysis continued for 15 minutes, when the copper is all deposited on the gauze cathode.   The electrodes are washed quickly with water, then with alcohol, dried and weighed.   The PbO_2 should be dried at above 200° C. to expel water.

FUSIBLE METALS, SOLDERS, ETC.

Alloys of Tin and Lead

Practically all solders are alloys of lead and tin in varying proportions.   To determine these two constituents only proceed as directed under Babbitt Metal, employing either scheme A or C.   A will be found simplest, and quite accurate when the tin is purified as directed in the note following the scheme. Demorest[1] purifies the tin precipitate by the use of ammonium sulphide as follows:

Two grams of the alloy are dissolved in nitric acid (sp. gr. 1.42) and evaporated to dryness.   To the residue 50 cc. of water and 5 cc. of HNO_3 are added, heated to dissolve the lead and filtered.   The metastannic acid on the filter is washed two or three times and then washed back into the beaker or flask in which the metal was dissolved.   25 cc. of NH_4HS (made by saturating NH_4OH (sp. gr. 0.9) with H_2S) are poured through the filter and into the flask.   This will dissolve all the metastannic acid and precipitate as sulphides the lead and copper which contaminated the tin.   The flask and its contents are heated and shaken for about

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[1] J. Ind. and Eng. Chem., March, 1910.

10 minutes and then the solution is poured through
the same filter as before, catching the NH_4HS
solution of the tin in a 300-cc. beaker. The sul-
phides on the filter are washed with water contain-
ing some NH_4HS. The filtrate is diluted to 200 cc.
The small amount of PbS and Cu_2S is dissolved in
a little nitric acid and added to the main solution
of lead and copper.

One hundred cubic centimeters of the tin solution
are pipetted off, 10 cc. of NH_4HS and 4 grams KCN
are added and the solution electrolyzed with a 5 to 6
ampere current, rotating the solution as described
on p. 171.

The solution of lead is diluted to 200 cc., 50 to
100 cc. (according to the amount of lead present)
are pipetted off, 15 cc. HNO_3 added, and the solu-
tion is electrolyzed, using a 5 to 6 ampere current
and rotating electrode.

Alloy of Bismuth and Copper

Dissolve 1 gram of the finely divided alloy in a
covered 400-cc. beaker with 10 cc. of dilute nitric
acid and evaporate to dryness on the steam bath.
Add a few drops of strong hydrochloric acid to the
residue and dilute somewhat with water. Let the
precipitate of bismuth oxychloride settle. Then
add more water and, if the solution remains clear,
filter off the precipitate. Wash and dry precipitate
as directed under Bismuth, p. 57. To the filtrate
add 8 cc. of strong sulphuric acid and evaporate
until white fumes of sulphuric acid are being freely
evolved. Cool, add 40 cc. of water and determine

copper either volumetrically as directed under Copper, p. 66, or add 2 cc. of strong nitric acid, dilute to 150 cc. and electrolyze as directed under Copper, p. 71.

Alloy of Lead and Bismuth

Dissolve 1 gram of the finely divided alloy in 20 cc. of dilute nitric acid in an evaporating dish. Evaporate on the steam bath to the consistency of sirup. Add a little water, stir thoroughly with a glass rod and evaporate again. Repeat this three or four times or until the addition of water fails to produce any further turbidity, which is a sign that the bismuth has been completely converted into the basic salt $Bi_2O_2NO_3OH$. A cold solution of ammonium nitrate (1 part NH_4NO_3 to 500 parts of water) is now added. Allow to stand for a short time. Stir frequently in order that all lead nitrate may go into solution. Filter off the basic bismuth nitrate and wash with the dilute ammonium nitrate solution. Dry, transfer as much of the precipitate as possible to a weighed porcelain crucible and ignite it with the ash of the filter. Heat gently at first, and then with the full flame of the Bunsen burner. Weigh as Bi_2O_3. $Bi_2O_3 \times 0.8965 = Bi$. As a check the Bi_2O_3 may be reduced to metallic bismuth with KCN as directed under Bismuth, p. 57. To the filtrate add 8 cc. of strong sulphuric acid, evaporate to fumes and determine lead as lead sulphate or volumetrically as directed under Lead, p. 88.

NOTE. — Swett[1] suggests the following method for separating bismuth from lead and tin: The acid filtrate from the mixed nitrates filtered from the tin oxide is treated with a moderate excess of potassium or sodium hydroxide solution. This precipitates the bismuth and cadmium if present, and redissolves the lead hydroxide.

The oxides are filtered off, washed, and dissolved in hydrochloric acid. The bismuth is precipitated in the well-known manner as basic chloride, by being poured into a large quantity of water.

By getting rid of the lead in the manner indicated there is no complication resulting from the precipitation of basic salts of bismuth where they are not wanted.

Alloys of Antimony, Tin, Lead, Bismuth, Cadmium and Zinc

The alloy is dissolved and then constituents are determined as in Babbitt metals, see sections, (a), (b) and (c) of scheme A (or the more elaborate scheme B). The tin nearly always contains some bismuth and lead, and should be purified as directed in the note to scheme A by fusion with sodium carbonate and sulphur.

Bismuth. — Evaporate the filtrate from the antimony and tin to sirupy consistency, add water and stir with a glass rod. Repeat the evaporation and add water, stirring as before. Do this a third time, when all the bismuth should be converted to insoluble basic $Bi_2O_2NO_3OH$. Now add a cold solution of ammonium nitrate (2 grams to the liter), allow to stand some time, stirring frequently, and filter. Wash with a cold solution of ammonium

[1] J. Ind. and Eng. Chem., Jan., 1910.

nitrate of the strength indicated and dry. Separate the filter and precipitate and burn the latter in a weighed porcelain crucible. Add the ash and ignite, gently at first, and finally with the full Bunsen burner flame. Weigh as Bi_2O_3. $Bi_2O_3 \times 0.8965 = Bi$.

Cadmium. — If not already done, evaporate the filtrate from the bismuth to 200 to 300 cc. and saturate with hydrogen sulphide. Filter and wash. Dry and separate the paper and precipitate. Place the latter in a large weighed porcelain crucible, cover with a watch glass and treat with dilute hydrochloric acid (1:1) on a water bath. As soon as evolution of hydrogen sulphide has ceased, wash the lower side of the watch glass off into the crucible, place the latter under the funnel, place the filter paper in the funnel and dissolve the precipitate which adheres to it in hydrochloric acid (1:1) and wash with hot water, catching the solution and washings in the crucible. Add a few cubic centimeters of dilute sulphuric acid (1:2) to the contents of the crucible and evaporate until SO_3 fumes are given off. Heat over a low flame until these cease to be given off, increase the temperature cautiously until the full Bunsen burner flame is used for a few minutes. Weigh as $CdSO_4$. $CdSO_4 \times 0.5392 = Cd$.

NOTE. — If copper is present the cadmium sulphide precipitate is dark. In this case proceed as above, except that the cadmium sulphate is only heated sufficiently to drive off all the SO_3. After weighing, the cadmium sulphate is dissolved in hot water to which a few drops of sulphuric acid have been added. Either sulphurous acid or ammonium bisulphite is added and ammonium sulphocyanate solution is dropped in with constant

stirring. After settling, the precipitate is filtered off on a weighed filter paper, washed, dried and weighed as $Cu_2(CNS)_2$. $Cu_2(CNS)_2$ $\times 0.5226 = Cu$. Calculate also to $CuSO_4$ and deduct from the mixed sulphate of copper and cadmium for $CdSO_4$. Copper can also be determined very easily in the filtrate from the bismuth electrolytically as directed in scheme A and the cadmium in the remaining solution by precipitation with hydrogen sulphide.

Zinc. — Boil the filtrate from the cadmium until all the hydrogen sulphide is expelled and determine the zinc as directed in (h), scheme A.

BRASS

Alloys of Cu, Sn, Pb, Zn, Fe, Al, Mn and P

Weigh 1 gram of the alloy into a small beaker and treat with 15 cc. of dilute nitric acid (2 nitric acid to 1 water). Cover immediately with a watch glass and when action becomes less violent heat to boiling until no more red fumes are given off. Dilute to 60 to 75 cc. and filter through a double filter paper. Wash, dry and separate paper from precipitate. Burn the former in a large weighed porcelain crucible, cool, moisten the ash with nitric acid and drive this latter off by cautious heating. Add the precipitate to the filter ash and ignite gently at first, and finally over the full flame of a Bunsen burner. Weigh as $SnO_2 + P_2O_5 +$ foreign oxides.

Tin. — To the contents of the crucible after weighing add six times as much of a mixture of equal parts of sodium carbonate and sulphur and heat over a small flame until the excess of sulphur is almost entirely removed, as is shown by there being no flame of burning sulphur between the

cover and the crucible. After cooling, treat the contents of the crucible with a little boiling water. The tin and some of the impurities also will go into solution. Add a little sodium sulphite until the solution becomes slightly yellow in color. This will reduce sodium polysulphide, in which oxides of iron and copper are soluble, to monosulphide, in which they are insoluble. The oxides remaining are filtered off, washed first with water containing 2 per cent sodium sulphite and finally with hydrogen sulphide water. Ignite and weigh. Subtract this weight from the weight of $SnO_2 + P_2O_5 +$ foreign oxides obtained above; the result will be $SnO_2 + P_2O_5$. To find the tin, determine the P_2O_5 as directed for Phosphorus and deduct from the weight of $SnO_2 + P_2O_5$. $SnO_2 \times 0.7881 = Sn$. The residue of foreign oxides should be small. Dissolve in a few cubic centimeters of strong hydrochloric acid, evaporate nearly to dryness and add to the main solution from the $SnO_2 + P_2O_5 +$ foreign oxides.

Lead. — Add 5 cc. of sulphuric acid (1:1) to the filtrate from the tin, etc., and evaporate until dense white fumes of SO_3 are given off. Cool and determine lead as directed in (d) or (e) of scheme A.

Copper. — Determine the copper as directed in (f), (g) or (h) of scheme A, in the filtrate from the lead.

If the alloy contains no manganese the following will be found an excellent method for determining both lead and copper by electrolysis. The operation is conducted exactly as in (h), scheme A, except that in place of the platinum rod used for an anode

a large weighed platinum crucible is employed.
The platinum crucible is held in place by a large
rubber stopper through the center of which passes
a copper or platinum wire which is bent up and
makes electrical connection with the crucible, being
forced against it by the stopper. The lead is
deposited upon the crucible as PbO_2, and is to be
washed with water and alcohol just as is the dish.
If manganese is present the deposit of $PbO_2 + MnO_2$
may be dissolved in hydrochloric acid, the solution
evaporated to dryness, 5 cc. of nitric acid and a
gram of lead peroxide added and the manganese
determined by comparison of the color produced
with that of a standard permanganate solution.
$PbO_2 \times 0.8643 = Pb$.

Aluminum. — Heat the filtrate from the copper
to boiling and add ammonia in distinct excess, boil
for five minutes and filter. Dissolve the precipitate
in as little hydrochloric acid as possible. Add to
the solution sodium carbonate solution until a
slight but distinct precipitate forms which fails to
redissolve on standing. Allow to stand fifteen
minutes and add at intervals of five minutes 1 cc.
of acetic acid (sp. gr. 1.033) until the precipitate
dissolves. Add ⁵ cc. of acetic acid in excess and
3 grams of sodium acetate. Dilute to 250 cc., boil
for five minutes, allow to settle and filter. Combine
the filtrate with that from the ammonia precipita-
tion, and determine manganese in the two. The
precipitate contains the iron and alumina. Dis-
solve in nitric acid, dilute to 150 cc., bring to a
boil and add ammonia in slight but distinct excess.

Boil for five minutes, allow to settle, filter, reject the filtrate, wash a few times with hot water, ignite and weigh as $Al_2O_3 + Fe_2O_3$. Determine the iron oxide as directed below and deduct from the weight of $Al_2O_3 + Fe_2O_3$ for Al_2O_3. $Al_2O_3 \times 0.5303 = Al$.

Iron. — Fuse the precipitate of $Al_2O_3 + Fe_2O_3$, after weighing, with potassium hydroxide in a silver crucible or dish. Treat the fusion with water, boil, filter and wash, dry, ignite and weigh the residue as Fe_2O_3. $Fe_2O_3 \times 0.7 = Fe$.

Or fuse the precipitate of $Al_2O_3 + Fe_2O_3$, after weighing, with sodium carbonate, dissolve in a little water to which a few cubic centimeters of hydrochloric acid have been added and drop into the solution a few small crystals of citric acid. Add ammonia until the solution smells slightly of it and then an excess of ammonium sulphide. Allow the black precipitate to settle, filter, wash a few times, dissolve in hydrochloric acid, add a little bromine water or a few drops of nitric acid, boil a while and add ammonia in slight but distinct excess. Filter, wash well with hot water, ignite and weigh as Fe_2O_3.

Manganese. — Evaporate the filtrate from the iron and alumina to about 200 cc., add enough bromine water to produce a good red color and evaporate slowly to 150 cc., adding bromine water when the solution becomes colorless. Filter and wash with hot water. If the precipitate is small, ignite and weigh as Mn_3O_4. $Mn_3O_4 \times 0.7202 = Mn$. If the manganese precipitate is considerable, boil with 10 cc. of nitric acid to which bromine water

has been added and treat the filtrate as directed
below: Redissolve the precipitate in 10 cc. hydro-
chloric acid (1:1), heat to boiling and add ammonia
to slight but distinct excess. Ignite and weigh as
Fe_2O_3. Calculate to iron and add to the iron found
above. To the ammoniacal solution add ammonium
phosphate solution in excess. Stir well. Allow to
stand two hours, filter, wash, ignite and weigh as
$Mn_2P_2O_7$. $Mn_2P_2O_7 \times 0.3872 = Mn$. Add the fil-
trate obtained by boiling the Mn_3O_4 with nitric
acid and bromine water to the main filtrate from
the Mn_3O_4.

Zinc. — Precipitate the zinc in the filtrate from
the manganese as directed in (*i*), scheme A, for
Babbitt metals.

Phosphorus. — Weigh 5 grams into a No. 3
beaker, add 25 cc. of concentrated nitric acid
and heat until nitrous fumes cease to come off.
Add 100 cc. of water, digest until all soluble salts
áre in solution and filter through a double filter.
Wash with water containing a little nitric acid.
Put the filter and precipitate ($SnO_2 + P_2O_5$) in an
Erlenmeyer flask and add 25 cc. of ammonium
sulphide. Digest on the ·steam bath or on the
cooler portion of the hot plate for one hour, shaking
frequently, filter and wash the paper free from
sulphides. Discard the filter. Add 20 cc. of
magnesia mixture to the solution and stir well.
Now add one-sixth the volume of the solution of
strong ammonia and allow to stand overnight. In
the morning filter, wash with cold water containing
one-sixth its volume of strong ammonia and 10 per

cent ammonium nitrate. Redissolve the precipitate in hydrochloric acid and wash paper free from acid. Add a few cubic centimeters of magnesia mixture to the solution and then ammonia, drop by drop, with constant stirring, until a precipitate forms. Now stir for five minutes and add one-sixth the volume of the solution of strong ammonia. Allow to stand overnight, filter, wash with ammonia mixture as above and ignite. Weigh as $Mg_2P_2O_7$. $Mg_2P_2O_7 \times 0.2784 = P$. If arsenic is present, it will be precipitated by the magnesia mixture also. In this case, after redissolving the precipitate in hydrochloric acid, pass hydrogen sulphide through the solution and filter off the arsenic sulphide. Boil the filtrate until free from hydrogen sulphide and precipitate phosphorus, as directed above, by adding a few cubic centimeters of magnesia mixture and then ammonia, etc.

Silicon. — Weigh 5 grams into a No. 4 beaker, add 5 cc. of concentrated nitric acid and 25 cc. of hydrochloric acid. Evaporate to dryness and bake for one hour in an air bath at 100° to 110° C. Cool, add 20 cc. of hydrochloric acid and 50 cc. of water, boil and filter. Wash the paper twice with hot water and then three times alternately with hot dilute hydrochloric acid (1:1) and hot water. Finish washing with hot water. Ignite over a blast lamp and weigh the residue. Moisten this with a drop of water and add a few cubic centimeters of hydrofluoric acid. Evaporate to dryness, ignite and weigh. The difference between the two weights represents SiO_2. $SiO_2 \times 0.47 = Si$.

Note. — When only small quantities of other elements than copper and zinc are present it will be found an excellent plan to dissolve 5 grams of the alloy in 5 cc. of nitric acid and 25 cc. of hydrochloric acid. When solution is completed add 30 cc. of dilute sulphuric acid (1:1) and evaporate until fumes of SO_3 come off. Cool, dilute to about 200 cc. and pass SO_2 gas through the solution. Add ammonium sulphocyanate until almost all of the copper is precipitated, as is shown by the blue color becoming very faint.

Filter and wash with hot water. Boil off the SO_2 from the filtrate and pass hydrogen sulphide into it to precipitate the tin, antimony, lead and also the copper left in the solution. Separate the tin and antimony from the copper and lead by digesting the precipitate with sodium sulphide, as directed in scheme B, and determine manganese, iron and aluminum as directed in the preceding paragraphs. Determine the zinc in the filtrate from the manganese. If much zinc is present, make this filtrate up to 1000 cc. and determine zinc in from 200 cc. to 500 cc. of it. To determine copper roast the sulphocyanide precipitate until the latter is decomposed. Dissolve the nitric acid, evaporate until most of the latter is expelled, add the solution to the filtrate from the lead, which contains some copper, make the combined solutions up to 1000 cc. and precipitate the copper in 100 cc. (= 0.5 gram of alloy) of this by battery as directed in scheme A.

Note. — If an alloy containing tin as one of its principal ingredients is dissolved in concentrated nitric acid, pure stannic oxide is not obtained, but it is contaminated with copper, lead and iron oxides, etc. According to Busse,[1] if nitric acid of a

[1] Zeit. f. anal. Chem., XVII, 53.

definite concentration is used to dissolve the alloy, pure stannic oxide remains insoluble. On the other hand, Treadwell and other authorities state that the tin dioxide is never pure and always contains small amounts of other oxides and must be purified by fusing with sodium carbonate and sulphur.

Mr. Price has found that for all technical purposes a brass which does not contain over 10 per cent of tin may be treated according to Busse and the stannic oxide obtained practically free from other oxides. Treat 1 gram of the finely divided alloy in a covered glass evaporating dish on the steam bath with 6 cc. of strong nitric acid, and add gradually 3 cc. of water. When the evolution of brown nitric oxide fumes has ceased, heat the solution to boiling and add 50 cc. of boiling water. Allow the precipitate to settle completely and filter through a Gooch crucible. Wash with hot water, ignite and weigh as SnO_2 as directed under Tin, p. 131. If there is any reason to doubt the purity of the precipitate, fuse with sodium carbonate and sulphur as directed in note, scheme A. The stannic oxide may be treated as directed under Tin, p. 131, and the tin determined volumetrically. To the filtrate add 2 cc. of strong sulphuric acid and evaporate to fumes. Dissolve in 30 to 40 cc. of hot water and filter off the precipitate of $PbSO_4$ on a platinum Gooch crucible. Wash, ignite and weigh as $PbSO_4$ as directed under Lead, p. 87. The lead may also be determined volumetrically as directed under Lead, p. 88. The copper in the filtrate may be determined volumetrically as directed under Copper, p. 66, or add 4 cc. of dilute nitric acid (1 : 1)

to the filtrate and determine copper electrolytically as directed under Copper, p. 71.

The lead and copper may be determined simultaneously by electrolysis in the filtrate from the precipitate of stannic oxide by adding 9 cc. of strong nitric acid and proceeding as described under Babbitt Metal, p. 168. In the filtrate from the copper precipitate the zinc as zinc pyrophosphate, as directed under Zinc, p. 140. Iron may be determined in a separate sample as directed under German Silver, p. 200, or if present in amounts exceeding 0.50 per cent may be separated as directed on p. 78. The zinc may also be determined electrolytically as follows: To the filtrate from the copper add 5 cc. of dilute sulphuric acid and evaporate until fumes are given off freely. Dissolve in 25 cc. of water and to the solution add 6 to 8 cc. sodium hydroxide solution (250 grams to the liter) until the zinc begins to precipitate as zinc hydroxide. Add ammonia until precipitate dissolves. Filter off any precipitate of ferric hydroxide present, wash with hot water and then with ammonia. To the solution or filtrate as the case may be, add glacial acetic acid until the solution is just acid. Electrolyze with a current of $ND_{100} = 0.5$ ampere and 4.8 to 5.2 volts. (See also method of Kemmerer, p. 146.)

Arsenic and Antimony. — It is sometimes necessary to determine small amounts of antimony and arsenic in brass. To determine arsenic, dissolve from 3 to 10 grams of the brass in a large platinum dish with sufficient nitric acid to dissolve or de-

compose it.   Cover the dish with a watch glass and heat until the alloy is dissolved or decomposed. When action has ceased, wash the watch glass and sides of dish, and evaporate nearly to dryness on the steam bath.   From this point proceed as directed for the volumetric determination of Arsenic, p. 51.   To determine antimony, treat 3 to 10 grams of brass in a 500-cc. Erlenmeyer flask with sufficient nitric acid to decompose or dissolve it.   If the alloy contains no tin or is low in tin add enough so that all the antimony will be precipitated.   When decomposition is complete, evaporate over a free flame until most of the nitric acid is expelled. Dilute to 300 cc., boil for ten minutes and let precipitate settle.   When solution has settled, decant as much as possible.   If the solution does not decant well, filter and return filter paper and precipitate to flask.   Then add 15 cc. strong H_2SO_4, 4 to 5 grams potassium acid sulphate and $\frac{1}{2}$ gram of tartaric acid.   From this point proceed as directed under volumetric determination of Antimony, p. 47.

BRONZE

Alloy of Copper and Tin

Determine the tin as directed under Brass, p. 180. To the filtrate add 2 cc. of strong sulphuric acid and evaporate to fumes.   The copper may be determined either electrolytically or volumetrically as directed under Brass.   Accurate results may also be obtained by treating 1 gram of the finely divided alloy with aqua regia and evaporating to dryness

the residue digested with sodium sulphide, and the tin determined electrolytically as directed under Tin, p. 137. The copper sulphide is dissolved in nitric acid and electrolyzed as directed under Copper, p. 71. Demorest's method described on p. 169 may also be used to advantage for bronze.

LEAD AND ZINC ALLOY

Dissolve 1 gram of the finely divided alloy in a covered glass evaporating dish with 5 cc. of strong nitric acid. When action has ceased, remove watch glass, add 2 cc. of strong sulphuric acid and evaporate to dryness on the steam bath. Dissolve in 30 cc. of hot water, filter off lead sulphate and treat as directed under Lead, p. 87. In the filtrate, precipitate zinc as pyrophosphate (see Zinc, p. 139). Lead may be determined electrolytically as follows: Dissolve 1 gram of the alloy in a 200-cc. electrolytic beaker in 15 cc. of strong nitric acid, dilute to 150 cc. and proceed as directed under Lead, p. 92. Zinc is determined in the filtrate as pyrophosphate, or a few cubic centimeters of dilute sulphuric acid added and the zinc determined electrolytically as directed under Brass, p. 188.

PHOSPHOR-BRONZE

Alloy of Copper, Tin, Zinc and Phosphorus

Dissolve 1 gram of the finely divided alloy in 6 cc. of strong nitric acid and 3 cc. of water in a glass evaporating dish. When action has ceased, filter off precipitate, which consists of a mixture of

stannic oxide, tin phosphate and small quantities of copper oxide.   Wash with dilute nitric acid and then digest it for twenty minutes by heating with a concentrated solution of sodium sulphide.   The residue, which consists of copper sulphide, is dissolved in nitric acid and added to the main solution. Determine the tin electrolytically by converting the sodium sulphide into ammonium sulphide as directed under Alloy of Antimony and Tin, p. 155. The phosphorus is determined in a separate 2 to 10 gram sample as directed under Phosphorus, p. 118. Determine the copper and zinc in the main solution as directed under Brass, p. 188.   The tin may be determined as stannic oxide by adding hydrochloric acid to the filtrate from the copper sulphide to acid reaction.   Allow to stand at a gentle heat until stannic sulphide and sulphur have settled. Filter, wash and treat precipitate as directed under Tin, p. 133.

MANGANESE-PHOSPHOR-BRONZE

Alloy of Manganese, Copper, Tin, Zinc and Phosphorus

The method of analysis is similar to that given for phosphor bronze with the exception that manganese has to be separated from zinc.   The manganese and zinc are separated by precipitating the zinc as sulphide with hydrogen sulphide in the presence of formic acid as described under Zinc, p. 140.   The manganese in the filtrate is determined either as pyrophosphate or volumetrically, as directed under Manganese, p. 103.

H. B. Swan[1] gives the following method for the analysis of manganese bronze.

The analysis of this well-known and important alloy necessitates the determination of tin, copper, iron, aluminum, manganese and zinc.   Tin, iron, aluminum and manganese are present in relatively small amounts, and inasmuch as the difference of a few tenths of one per cent of these ingredients may materially alter the physical properties of this bronze, it is extremely important at times to have accurate and reliable results.   The method outlined below has been worked out in this laboratory; it has given excellent results and is comparatively rapid, a period of about six to seven hours being required for the complete analysis.

A 5-gram sample of drillings is weighed out into a No. 2 beaker, 20 cc. of water added, and then, carefully, 20 cc. of HNO_3 (sp. gr. 1.42).   Cover, and after the reaction has subsided, heat to complete solution and boil for about five minutes. This strength of acid has been found most satisfactory, as in using a more dilute solvent the precipitate of metastannic acid runs through even a double filter.

Filter off the precipitate of metastannic acid through a double filter of "S & S" No. 589 white ribbon paper, using a platinum cone and employing suction.   Wash the precipitate well with half and half nitric acid and allow the suction to act sufficiently long after the paper is drained to dry it somewhat. Ignite the precipitate and paper together, charring

[1] Met. and Chem. Eng., August, 1910.

carefully, and afterwards raising the heat to the full heat of a Bunsen or Tyrell burner. Calculate the tin from the precipitate of SnO_2. It is not necessary to subject this precipitate to any further treatment to purify it, as it is so small that only traces of iron or manganese can be precipitated along with the tin.

To the filtrate is added 5 cc. of concentrated H_2SO_4 (sp. gr. 1.84) and the whole evaporated on the hot plate or bath almost to dryness. This is to free it from nitric acid, and occasionally, if a low-grade spelter is used in the manufacture of the alloy, to precipitate any lead present.

If there is an appreciable amount of lead present and it is desired to determine it, after cooling the crust of sulphates in the bottom of the casserole, about 50 cc. of water are added when the sulphate is filtered off onto an asbestos pad in a platinum Gooch crucible, washed with a 5 per cent solution of H_2SO_4, then, after removing the filtrate, washed with alcohol in a clean flask. The crucible is then ignited at a low heat, but sufficient to remove any H_2SO_4 that may still be present. The filtrate is then transferred to a 500-cc. graduated flask and diluted to 500 cc.

For copper either pipette off 100 cc. or measure out, by means of a 100-cc. graduated flask, 100 cc. of the solution, and put into a tall non-lipped 150 cc. beaker. Just neutralize with NH_4OH and then add about 3 cc. of a mixture of three parts nitric (sp. gr. 1.42) to one of sulphuric acid (sp. gr. 1.84) and submit the solution to electrolysis. Mr. Swan uses

a gauze cathode and a rotating anode and employs a current of $ND_{100} = 3/5$ amperes. After testing with H_2S on a spot plate to insure the complete removal of the copper, the cathode is washed as it is removed from the solution and, after removing, with H_2O and then dipped in alcohol and dried. A quick and very satisfactory method of drying consists in holding the cathode above a piece of asbestos covering the top of a Tyrell burner, and at the same time allowing a current of compressed air (not too strong) to play over the gauze.

Two 100-cc. portions of the solution are run simultaneously, and after the removal of the copper, iron is determined in one portion and aluminum in the other. To òne portion add 5 grams of ammonium chloride, make just slightly alkaline with NH_4OH and heat to the boiling point. Cool, allow to settle and filter. Iron and aluminum are precipitated. Wash with dilute ammonium chloride solution. The precipitate is redissolved in 5 cc. of HCl (sp. gr. 1.12) and the solution diluted up to 400 cc. in volume. Add 10 cc. of a 10 per cent solution of sodium ammonium hydrogen phosphate and the NH_4OH till just a slight but permanent precipitate forms. Then add $1\frac{1}{2}$ cc. of strong HCl and then 10 to 15 cc. of a 20 per cent solution of sodium thiosulphate. Heat to boiling, and after the boiling point is reached add a mixture of 15 cc. of a 20 per cent solution of ammonium and 8 cc. of strong acetic acid. Boil for about ten minutes, allow to settle and filter. The precipitate filters readily, but is hastened by using suction. Wash

several times with hot water. The paper and precipitate are burned together and then ignited over the blast lamp, in either a porcelain or platinum crucible. Weigh as $AlPO_4$, the conversion factor being 0.2219 for aluminum.

The iron, aluminum and manganese are precipitated together in the other 100-cc. portion with NH_4OH, the precipitate dissolved in about 5 cc. of strong HCl, the iron reduced with stannous chloride and then titrated with a solution of N/10 $KMnO_4$, using a guard solution made by mixing phosphoric acid, manganese sulphate and sulphuric acid together. For details of this method see Blair's "The Chemical Analysis of Iron."

Now two other 100-cc. portions of the solution are used for the determination of manganese and zinc. The copper may ·be removed either with metallic aluminum or by electrolysis. In the latter case the copper is removed from the sulphuric acid solution without the addition of ammonia or nitric acid but adding about 1 cc. of H_2SO_4 for a total volume of 125 cc. of solution.

After removing copper, for manganese add a few cubic centimeters of strong bromine water, make ammoniacal and then add a slight excess. Heat till all the iron, aluminum and manganese are precipitated, then filter, wash and dissolve in a few cubic centimeters of sulphurous acid. Now add to the solution 10 cc. of HNO_3 and 30 cc. of H_2O and boil a minute, then add about $\frac{1}{4}$ gram of sodium bismuthate and heat till the pink color completely disappears. Add a few drops of sulphur-

ous acid to clear the solution and boil again to expel all nitrous fumes. Cool the solution till quite cold and add a slight excess of sodium bismuthate again.   Agitate a minute or two, then add 50 cc. of 3 per cent HNO_3 and filter through asbestos on a platinum cone, using suction, wash with 50 cc. more of 3 per cent HNO_3, add an excess of ammonium sulphate solution and titrate the excess with a solution of $KMnO_4$ which has been standardized against the ferrous ammonium sulphate solution. See p. 104.

Zinc is determined in the other portion of the solution from which the copper has been removed, without the addition of nitric acid.   Zinc may be estimated either as the pyrophosphate, which is the more accurate method, or by electrolysis, which is more rapid but not quite so accurate.   For the details of both methods see section on Zinc, p. 139.

If the electrolytic method is selected, the zinc is plated out from the solution made sufficiently alkaline to redissolve the precipitated zinc and aluminum.   The iron which is precipitated along with the zinc and aluminum by the sodium hydrate is filtered off before the electrolysis is proceeded with. It is best to boil the alkaline solution to free the iron hydrate from any zinc.   The filtrate from the iron is then cooled and the zinc plated out on a copper-plated cathode by the use of a rotating anode.

GERMAN SILVER, WATCH NICKEL AND NICKEL ALLOYS

Alloys of Nickel with Cobalt, Copper, Zinc, Iron,
Manganese, etc.

The method of estimating nickel by means of adding potassium cyanide to an ammoniacal solution of nickel containing silver iodide in suspension, so that the solution remains turbid until the nickel is all converted into the double cyanide of nickel and potassium, after which a single drop of the cyanide in excess will clear up the solution, was originally proposed by T. Moore, and modified by Mr. Price for use in German silver, etc.

The following elements interfere with the method: manganese, zinc, iron, aluminum and especially copper, which owing to its forming cyanides renders the process valueless. Cobalt if present will be estimated as nickel.

The iron, aluminum and zinc may be kept in solution so that they do not interfere, by using organic acids, such as tartaric, citric, etc., or sodium pyrophosphate. The copper may be separated from the zinc, nickel, etc., by any of the well-known methods.

C. M. Johnson[1] found that nickel could be determined in the presence of manganese by the use of a large amount of citric acid (24 grams citric acid to 1 gram of the alloy), 0.25 per cent of nickel being detected in the presence of 95 per cent of manganese. The authors have no experience with this method,

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[1] J. Am. Chem. Soc., 8, 1201, 1907.

as the amounts of manganese found in German silver rarely exceed 0.50 per cent, and are determined simultaneously with the copper, by electrolysis. The following analysis of a leaded German silver will illustrate the method.

Lead. — Dissolve 1 gram of the alloy in 5 cc. of nitric acid (sp. gr. 1.42) in a glass evaporating dish, covered with a watch glass, on a steam bath or hot plate. When action ceases wash down watch glass and add 2 cc. of sulphuric acid (sp. gr. 1.84). Evaporate until white fumes are given off, take up in hot water, filter into a weighed platinum Gooch crucible, wash with a solution of distilled water containing 10 cc. of sulphuric acid (sp. gr. 1.84) and 10 cc. of alcohol to the liter. Ignite for five minutes, resting the crucible on a platinum crucible cover. Cool and weigh as $PbSO_4$. $PbSO_4 \times 0.6829 = Pb$.

Provided the alloy contains no manganese it may be dissolved directly in 15 cc. of nitric acid (sp. gr. 1.42) in a 200-cc. electrolytic beaker, and the lead and copper deposited simultaneously by electrolysis. Dilute the solution to 150 cc. with distilled water and electrolyze with a current of $ND_{100} = 1$ to 1.5 amperes and 1.4 volts. The lead will all be precipitated in the course of an hour upon the anode, and the copper will be deposited at the same time on the cathode. The lead separates first, and the copper more slowly. When the lead is fully precipitated, wash with water and alcohol and dry for fifteen minutes at a temperature from 200° to 230° C. Cool and weigh. $PbO_2 \times 0.8643 = Pb$.

Copper. — Neutralize the solution with ammonia and add 5 cc. of nitric acid (sp. gr. 1.42) and 2 cc. sulphuric acid (sp. gr. 1.84) and electrolyze with a current of $ND_{100} = 0.5$ ampere and 2 volts, until copper is fully precipitated. Wash with water and alcohol, dry, cool and weigh. Increased weight is metallic copper.

Copper and Manganese. — In this case it is assumed that manganese is present. To the filtrate from the lead sulphate add 2 cc. of dilute nitric acid (1:1). If more than 3 or 4 per cent of nitric acid is present the manganese will not all be precipitated on the anode, but will remain in solution, and a red color will appear at the anode, due to the formation of permanganic acid. Electrolyze with a current of $ND_{100} = 0.5$ ampere and 2.5 volts. The manganese will be deposited upon the anode as dioxide and the copper will be deposited at the same time on the cathode. (The electrodes used by the authors consist of two cylinders, one fitting inside the other.) Wash the manganese dioxide on the anode with water and alcohol, dry and ignite. The dioxide will be converted into Mn_3O_4. $Mn_3O_4 \times 0.72026 = Mn$. Wash the copper on the cathode with water and alcohol, dry, cool and weigh. The increase in weight is metallic copper.

Nickel. — After removal of copper and manganese, transfer the solution containing the iron, nickel and zinc to a 400-cc. beaker. Add from 3 to 4 grams of ammonium chloride and then 50 to 75 cc. of a solution of sodium pyrophosphate containing from 10 to 15 grams of Merck's pure crystals.

Make up this solution just before using, and use a quantity depending upon the amount of zinc present. Neutralize with ammonia and then add enough to make the solution only slightly but yet distinctly alkaline.   A large excess of ammonia will hinder or entirely prevent the reaction.   Cool and do not let temperature of the solution get much above 20° C., or the result will be irregular.   Add 2 cc. of a 10 per cent solution of potassium iodide and titrate with a standard solution of potassium cyanide containing silver nitrate, until the white cloud caused by the formation of silver iodide has entirely disappeared and one drop of the cyanide causes a clear solution.   This is the end point, which is very sharp and distinct.   The following reactions take place:

(1) $Ni(NO_3)_2 + 4\,KCN = Ni(CN)_2\,2\,KCN + 2\,KNO_3.$
(2) $AgNO_3 + 2\,KCN = AgCN \cdot KCN + KNO_3.$

The turbid white cloud in the solution is caused by the precipitate of silver iodide, which is almost insoluble in weak ammonia, and this turbidity will increase up to the point where the formation of the double cyanide of nickel and potassium is complete, when the slightest excess of cyanide will clear up the solution.

The zinc is usually determined by difference and the iron in a separate sample as follows: Take 1 gram of the alloy, dissolve it in 10 cc. of nitric acid (sp. gr. 1.42) in a 250-cc. beaker; then, after solution is complete, add 10 cc. of hydrochloric acid (sp. gr. 1.19) and 7 grams of ammonium chloride, dilute with water to 100 cc. and heat to boiling,

precipitate with ammonia, filter, wash with hot water, place a 300-cc. flask containing 5 grams of C. P. zinc under the funnel and dissolve the ferric hydroxide with a hot solution of 10 cc. hydrochloric acid (sp. gr. 1.19) and 20 cc. water. When action has nearly ceased, add a solution of 10 cc. sulphuric acid (sp. gr. 1.84) and 20 cc. water, which will dissolve the remainder of the zinc and insure a sharp end point with the potassium permanganate. When zinc is all dissolved, fill the flask up to the neck with cold water, and cool under the tap to room temperature. Transfer to a 400-cc. beaker and titrate with standard solution of potassium permanganate. If it is considered necessary to determine zinc other than by difference, the zinc and nickel can be separated in the following manner: Evaporate the solution left after removal of copper by electrolysis (in order to save time the copper may be precipitated and separated from the zinc, nickel, etc., by metallic aluminum, hydrogen sulphide, or any other of the well-known methods) to small bulk and nearly neutralize with sodium hydroxide. Pour the solution containing zinc, iron and nickel slowly, with constant stirring, into 60 cc. of a 10 per cent solution of sodium hydroxide, then add 60 cc. of distilled water, and filter. Dissolve precipitate in as little hydrochloric acid as possible, and repeat precipitation with 60 cc. of a 10 per cent solution of sodium hydroxide. Combine the filtrates, which will contain the zinc. Dissolve the nickel and ferric hydroxide in dilute nitric acid, then add 2 cc. of concentrated sulphuric acid.

The presence of the sulphuric acid insures a sharper end reaction with the potassium cyanide solution. Add ammonium chloride, sodium pyrophosphate, etc., and titrate with a standard solution of potassium cyanide as described before.

Owing to the fact that zinc is not present in this case, it is necessary to add only about one-quarter of the amount of ammonium chloride and sodium pyrophosphate or just enough to hold the iron in solution. Acidify the combined filtrates containing the zinc with formic acid, heat to about 80° C., and pass in hydrogen sulphide. As soon as the zinc is all precipitated, filter and wash with hot water. Dissolve the zinc sulphide in hydrochloric acid and boil to expel hydrogen sulphide. Make faintly alkaline with ammonia, then faintly acidify with hydrochloric acid, and then add 3 cc. in excess of concentrated hydrochloric acid. Dilute to 250 cc., heat to nearly boiling and titrate with a standard solution of ferrocyanide until one drop of the solution tested on a porcelain plate with a drop of a 15 per cent solution of uranium acetate shows a brown tinge.

Reagents. — Standard solution of potassium cyanide containing silver nitrate. This solution should contain 25 grams of pure potassium cyanide and 1.25 grams of silver nitrate to the liter. Many of the commercial cyanides contain sulphur, which causes a darkening of the solution when titrating, due to the formation of silver sulphide. If pure cyanide is not obtainable, the sulphur impurity may be removed by thoroughly agitating the cyanide solution with oxide of bismuth.

Potassium iodide, 10 per cent solution. Sodium pyrophosphate. Merck's pure crystals. Ammonium chloride, the C. P. salt.

Standardization.—The solution is standardized on a solution of known nickel contents. The authors use crystallized, C. P. nickel sulphate. Dissolve about 4 grams in a 400-cc. beaker. As all nickel sulphate contains iron as an impurity, it must be removed before electrolyzing solution for nickel. After removal of iron transfer solution to a carefully graduated 500-cc. flask. Dilute to the mark with water, and after thoroughly mixing the solution remove two 50-cc. portions with a pipette, transfer to two 200-cc. electrolytic beakers. Add 2 cc. sulphuric acid (sp. gr. 1.84), neutralize with ammonia, add 40 cc. of ammonia (sp. gr. 0.90). Electrolyze with a current of $ND_{100} = 0.5$ ampere and 2.5 volts.

After the nickel is all precipitated, wash with water and alcohol, dry and cool. The increase in weight gives the actual nickel contained in 50 cc. of solution. A solution of this strength should contain about 0.1 gram of nickel and should contain enough free acid to prevent the formation of any precipitate on the addition of ammonia to alkaline reaction. If a precipitate forms, add a little ammonium chloride and it will clear up.

Take 50 cc. of the solution in a pipette and transfer to a 400-cc. beaker, dilute to 200 cc., make slightly alkaline with ammonia, add a few drops of potassium iodide and titrate with potassium cyanide solution, adding it slowly, until one drop causes the white cloud entirely to disappear.

Example. — If 50 cc. of the solution contained 0.0905 gram of nickel and it took 20.3 cc. of potassium cyanide to produce a clear solution, then 1 cc. of potassium cyanide would be equivalent to 0.00445 gram of nickel. It is surprising that this method has not come into more general use, combining as it does extreme accuracy and great rapidity with ease of manipulation. After the removal of the copper, the total time consumed in determining the nickel should not exceed twenty-five minutes. When one considers that it enables the operator to dispense with the usual tedious separation of zinc and nickel, the superiority of the method in the analysis of German silver is very apparent.

NOTE. — The following scheme may also be employed for the analysis of German silver: Dissolve one gram of the alloy in 15 cc. of a mixture of 2 parts concentrated nitric acid and 1 part water. After all action ceases, evaporate to about one-half its bulk, and if any residue remains filter off and weigh as tin (see (*a*), scheme A). Determine copper in the solution by electrolysis as directed in scheme A. To the solution, after the copper has been removed, add sodium carbonate until the solution is slightly alkaline and precipitate the iron as directed in scheme D.

Nickel. — Evaporate the solution to small bulk and nearly neutralize any acid with sodium hydroxide. Dissolve 5 grams of caustic soda in 50 cc. of water and pour slowly into this, with constant stirring, the solution containing the nickel and zinc. Dilute the solution with an equal bulk of water and filter. Redissolve the precipitate in a little hydrochloric acid, nearly neutralize and again pour into a solution containing 5 grams of sodium hydroxide. Dilute and filter. Combine the filtrates and determine the zinc in them as directed below. Dissolve the precipitate of nickel hydroxide in dilute sulphuric acid and wash the paper free from acid.

The solution should measure about 100 cc.   Add 5 grams of ammonium sulphate and 40 cc. of concentrated ammonia.   Electrolyze overnight as directed for copper in scheme A.   The nickel is deposited as the metal.

Zinc. — Acidify the solution with acetic acid, heat to boiling and pass a current of hydrogen sulphide through the liquid.   When all the zinc is precipitated, allow the sulphide to settle, filter and wash.   Dissolve the precipitated zinc sulphide in hydrochloric acid and boil until hydrogen sulphide is expelled and precipitate zinc as directed in scheme A, p. 162.

SPELTER

Rapid Determination of Iron and Lead in Spelter. — In sampling spelter it is customary to take three or four slabs from each car of the shipment.   Two holes are drilled in each slab about four inches from the ends in order to allow for the segregation of lead in the slab.

The drill should be run at a slow speed and with a slow feed in order to obtain drillings which will dissolve readily in the acids used.   Pass a magnet through the drillings before weighing in order to remove any particles of iron that may have become mixed with the spelter.   Failure to do this is often the cause of annoying discrepancies in the results of different chemists.

The method commonly employed in analyzing spelter is to dissolve the zinc in a mixture of either sulphuric acid and water or hydrochloric acid and

water. In either case zinc only goes into solution, the other metals, with the exception of arsenic and antimony, being left as spongy masses. The sample is generally weighed in the afternoon and allowed to stand overnight at ordinary temperature until all action has practically ceased. It is then filtered and washed with hot water. The filtrate contains the iron.

The solution is boiled, then cooled to room temperature and titrated with a standard solution of potassium permanganate. In case the iron has become oxidized to the ferric state it is reduced by 5 grams C. P. zinc in which the amount of iron is known and deducted from the total iron found. The residue on the filter contains the lead, which is digested with nitric acid. Sulphuric acid is then added, the solution evaporated to fumes and the lead determined either as lead sulphate, or sodium acetate and acetic acid are added and the solution titrated with a standard solution of ammonium molybdate. Owing to an increasing demand for greater speed and higher accuracy the following rapid method was devised by Mr. Price. It has been in use for some little time, and has given such good satisfaction that the authors thought it might prove helpful to others engaged in the same line of work.

Lead. — Weigh out 5 grams of spelter into a 400-cc. beaker, add a few cubic centimeters of water, cover with a watch glass and dissolve in 20 cc. nitric acid (sp. gr. 1.41 to 1.42), adding it 10 cc. at a time on account of the violent action. When action has

ceased and the zinc is dissolved, which will take only two or three minutes, wash the watch glass and sides of the beaker with distilled water, transfer solution to a 200-cc. electrolytic beaker and dilute with distilled water. The volume of the electrolyte should be 150 cc. and its temperature 50° to 60°. Electrolyze with a current of $ND_{100} = 1$ to 1.5 amperes and 2.5 volts.

The anodes are platinum cylinders 2 inches long and 1 inch wide and having a stem of heavy wire 4 inches above the cylinder, making the total height 6 inches. To obtain the best results the anodes should be roughened with the sand blast. The cathodes are heavy platinum wires, 6 inches long, with spirals at the ends. In the course of an hour all the lead will have been precipitated upon the anode. Wash the latter without interrupting the current. Wash with water and alcohol and dry for fifteen minutes at 200° to 230° C. If the deposit is not dried for this length of time and at the above temperature it will weigh too much, due probably to included water, which is expelled with difficulty.

Mr. Price has found, as did Prof. E. F. Smith, that the factor to multiply the dioxide by to get the lead value should be 0.8643 instead of 0.866. Any zinc that may form on the cathode can be disregarded, as it has no effect upon the deposit of PbO_2 on the anode. This can be entirely avoided by using a small cylinder 2 inches long and $\frac{1}{2}$ inch wide as a cathode instead of the heavy platinum wire. The PbO_2 deposit can be readily removed

by covering the anode with a solution of dilute nitric acid and inserting a rod of copper.

Iron. — Weigh 5 grams of spelter into a 10-ounce flask. Treat with a mixture of 10 cc. of strong hydrochloric acid and 20 cc. of distilled water. When strong action has ceased, add gradually a mixture of 10 cc. strong sulphuric acid and 20 cc. distilled water. This should dissolve most of the zinc remaining and secure a sharp end point with the potassium permanganate. When the zinc is all dissolved, fill the flask to the neck with cold distilled water and cool to room temperature. Filter off the black residue, which contains lead, using a plated filter, on which it is advisable to sprinkle some granulated zinc to prevent oxidation. If the lead were not filtered off it would consume permanganate, and cause trouble by increasing the percentage of iron. Dilute the filtrate to 400 cc. Titrate the filtrate with a standard solution of potassium permanganate containing 1.118 grams of $KMnO_4$ per liter until a very faint permanent pink color is obtained. One cubic centimeter of this solution will oxidize 0.002 gram of iron and, on the basis of 5 grams taken, 1 cc. = 0.01 per cent of iron. Its exact value may be found by standardizing in the usual way with metallic iron. The complete analysis of the spelter for lead and iron should not take over an hour and a half, and the number of the determinations possible is limited only by the number of units at hand.

REFINED COPPER ANALYSIS [1]

The percentage of the principal metal in matte, pig, anodes and refined copper is determined in technical laboratories either by titration or by electrolysis, and the method should be suited to the character of the material treated. Although a quick titration may be preferred for low-grade ores and mattes, it does not permit as close work, according to the writer's experience, on 99 to 100 per cent copper. The margin of difference between the standard and the sample is too narrow, and possible errors in titration are too large to permit results accurate within a limit of error of 0.05 per cent on " converter " or 0.01 per cent on " refined " copper.

The complete deposition of copper may be proved by testing 1 cc. of the copper solution with hydrogen sulphide water on a porcelain tile.

0.005 mg. of dissolved metal in 1 cc. will impart a distinct brown tint, and electrolysis is thus theoretically and practically an absolute method, yielding the total metal in metallic form for exact weight.

The impurities commence to deposit generally after some hours, when the solution has become colorless, while the deposition of the last traces of copper, particularly from the solution of a 5-gram sample, is not complete for several hours, until some hydrogen is evolved from the cathode and most of the free nitric acid present has been converted to ammonium sulphate.

From this fact the old, oft-quoted test, which

[1] George L. Heath, J. Am. Chem. Soc., Vol. XXVI, No. 9, 1904.

directs that the dish or beaker shall be filled up a little and the color of the upper portion of the plate noted after a short interval, must be condemned as not accurate, at least for concentrated solutions.

If the electrolytic assay can be made applicable to impure copper, it will permit closer agreement and more absolute work, if accuracy is desired rather than the saving of time.

A. H. Low devised a method for the volatilization of arsenic only, from ores by means of a solution of sulphur in bromine.   The writer succeeded in removing antimony with the same reagent, applied to the chlorides, and by subjecting the residue to a high heat.   The operation is too tedious and offensive to be practical.

It is very unfortunate that the many experimenters on electrolytic separations have taken such small quantities for their published researches.   In practical technical work the necessity of securing a fair sample makes the selection of at least 0.5 gram of matte and generally from 1 to 5 grams of copper an imperative necessity.

Duplicate 5-gram samples of refined metal ought to check within 0.02 per cent, and the allowable error in the weighing alone may be assumed as 0.01 per cent and 0.0001 gram on the scales.

In theory this requires a sample of 5 grams to permit work within the above specific limits of error.

E. F. Smith describes a method for the electrolysis of arsenical copper in ammoniacal solution. The principle has been variously modified by Smith, Oettel, Rüdorff and McCay.

The writer will describe another modification and three original methods devised in order to adapt the principle of electrolysis to any class of copper produced by refineries.

The beaker is 5.4 cm. ($2\frac{1}{8}$ inches) in diameter and about 12.7 cm. (5 inches) high, and is always kept covered with split glasses to prevent loss by spattering.   The writer always deposits the silver with the copper.   Before weighing a sample of drillings a strong magnet should always be passed carefully through the drillings to remove iron.

Annoying discrepancies between chemists may have been partly due to neglect of this precaution.

METHOD I

Details. — The following process is adapted to the assay of metal containing arsenic and antimony but less than 0.01 per cent of nickel plus cobalt plus zinc, which would be at least partially deposited.

Dissolve 5 grams of refined metal (or 1 gram of low-grade material) in 20 cc. of strong chemically pure nitric acid (or 10 cc. for 1 gram copper) and evaporate at a gentle heat with 10 cc. concentrated sulphuric acid until the residue is white and smells sweet, or free from nitric acid.   Dissolve in 70 cc. of distilled water, add 1 cc. nitric acid and just sufficient excess of ammonia to redissolve the basic copper and form a clear alkaline solution.   Cover the beaker and electrolyze.   As soon as the solution is colorless, wash down covers and sides of the beaker with a fine jet.   When the cathode commences to show bubbles of hydrogen, remove 1 cc.

of solution with a medicine dropper to a porcelain tile and test, first acidifying with a drop of dilute sulphuric acid. The time may be much shortened by the employment of a very high initial voltage, 3.8, and amperage, $ND_{100} = 2.5$, for about six hours, or until the solution takes a paler purple color and the Cu starts to deposit rapidly. Then lower current gradually to $ND_{100} = 0.35$; voltage $= 2.5$. The check results given are on a copper (A) containing 0.260 per cent of arsenic and traces of antimony, and show the agreement which can be obtained in spite of the segregation of impurities possible in such material: 99.63 per cent; 99.64 per cent; copper (+ silver). Time, sixteen to eighteen hours.

The chemists of the International Nickel Company are understood to have proved that the platinum anode spirals will not be appreciably attacked by ammonia if old, very soft and pure wires are selected.

METHOD II

This method may be used for copper containing only traces of antimony and less than 0.02 per cent arsenic but large amounts of selenium or tellurium.

Dissolve the sample of copper in nitric acid, as previously directed, and evaporate with 6 cc. of sulphuric acid until the residue is white. Dissolve in 60 cc. of water and wash into a lipped beaker, placing the first beaker under a funnel fitted with a 3-cm. filter. Heat solution nearly to boiling and saturate with a current of sulphur dioxide for ten minutes. The gas must be free from chlorine,

generated from refined copper and pure sulphuric acid. Settle overnight, filter into the original beaker and wash with a little hot water. Boil off the sulphurous acid. Ignite the filter in a porcelain crucible to a red heat, redissolve the residue in 1.5 cc. nitric acid, wash into the copper solution and electrolyze. Have the final volume of the solution sufficient to cover the electrode — about 120 cc. Current ND_{100}, 0.3 to 0.4 ampere; voltage, 2.2; time, thirty hours; results are accurate. Check samples (B) of a seleniferous pig copper assayed 99.78 and 99.79. A sample of only 1 gram will evidently require much less time for electrolysis.

METHOD III

For Metal Carrying over 0.01 per Cent Antimony and Other Elements. — The details of this method were worked out by Mr. A. W. Senter and involve more personal manipulation, but will accomplish the removal of much antimony in addition to the other impurities.

Dissolve the copper and evaporate with sulphuric acid as usual. Redissolve in 70 cc. water and add a measured quantity of a solution of pure nitrate of iron (1 cc. = 0.01 gram of metallic iron). For 1 gram of copper use 1 cc. ferric nitrate, or 3 cc. for 5 grams of metal. Wash into a lipped beaker and place original beaker under a funnel fitted with a small paper filter. Precipitate the iron from the hot solution with ammonia, filter and wash out salts. Place the solution on a hot plate to concentrate, reprecipitate iron from dilute sulphuric

acid solution, preserving the filtrate, dissolve the iron again and pass hydrogen sulphide gas. Filter on the same filter, extract with a very little hot dilute sodium sulphide, pouring it back and forth through the filter. Ignite filter and contents in a porcelain crucible, redissolve in 1.5 cc. of strong nitric acid and add to the main solution, which has been acidified with sulphuric acid and diluted, or concentrated, to the proper final volume. Results: Sample (A), 99.64; sample (B), 99.78. Current ND_{100}, 0.35 to 0.45 ampere; voltage, 2.2 to 2.4; time, about thirty hours for 5 grams of metal.

METHOD IV

The principle of this has just been discovered as the result of various experiments to find a salt which would prevent deposition of arsenic and antimony.

It is rapid and accurate in its proper field and peculiarly adapted to several commercial brands of copper containing much arsenic but not over 0.005 or, at most, 0.01 per cent of antimony. In the latter case, to avoid contamination of the large cathode, the last traces of copper had better be taken out with a narrow 1-inch cathode, if antimony commences to show on the copper. If much selenium or tellurium is present with the excessive arsenic, remove them first by Method II. Dissolve 5 grams of copper in nitric acid, dilute to 50 cc. and add only 3 cc. of concentrated sulphuric acid. Add ammonia until a slight permanent precipitate forms and redissolve this by exactly 1 cc. of sulphuric acid (sp. gr. 1.84) to prevent deposition of

nickel or zinc. Now stir in dry, powdered, chemically pure ammonium nitrate (free from traces of chlorine) until the solution is thoroughly saturated and a little remains undissolved. Electrolyze with a current of $ND_{100} = 0.7$ ampere and 2.7 to 2.8 volts for twelve hours, then reduce to 0.5 ampere. The total time for a 5-gram sample is about thirty hours. Test as usual with hydrogen sulphide water. Any trace of copper will show at once; arsenic a little later. Results: Sample (A), 99.64 per cent; in presence of 0.1 per cent antimony, black plate, 99.88 per cent.

After removing the large cathode, test the solution with a small cathode, if the end point is doubtful. If the solution is too acid, the copper will not deposit properly, but a trace of free acid is necessary.

Less time and chemicals should be allowed for in any of these methods if only 1 gram of copper is taken for the assay.

One or the other of the plans devised may be selected so as to permit accurate control work with any brand of metallic copper.

Methods for the Complete Analysis of Refined Copper

In 1894 Dr. H. F. Keller presented a paper on the analysis of copper as practiced by him at that time, and similar condensed accounts on Montana methods appeared from the pen of Titus Ulke in 1899. In response to invitation, the writer will present the principal methods now employed in large technical laboratories, giving preference to those which are personally believed to be most

delicate and accurate, condensing the account by reference wherever possible.

Great accuracy both in sampling and in chemical manipulation is especially necessary in the case of copper on account of the precious metals it frequently contains, and on account of the marked effect which even traces of some impurities have on its physical properties, and because of the liability of those impurities to segregation on cooling from a fluid to a solid state.

No technical chemist would now go through the tedious extraction of vast quantities of sulphide of copper as originally proposed by Fresenius. The present tendency is to take separate samples for the estimation of each group of foreign elements by some special method of isolation. Analytical results are usually carried out to 0.0001 per cent.

Sampling

When copper is to be assayed for gold and silver, the material should be sampled direct from the molten furnace charges after thoroughly mixing and agitating the bath by the refining process.

A thin square plate, $6 \times 6 \times \frac{1}{2}$ inches, to represent the lot, is carefully poured from a full ladle. The size might be increased to $9 \times 9 \times \frac{3}{4}$ inches for very rich material. A set of five $\frac{5}{16}$-inch holes drilled through the half-inch plate will furnish an assay ton (29 grams) sample for assay for silver and gold. The drillings from one hole of $\frac{1}{4}$ inch diameter will give one sample for electrolytic copper assay. Duplicates are generally taken. The holes should

be bored at a distance from the edges of at least three times the thickness of the plate.

Edward Keller's admirable research fully explained the principles of sampling in detail and proved the foregoing to be the rational method of procedure. Commercial reasons, however, make it necessary for custom works to sample an immense amount of western metal in the form of pigs, slabs and anodes. These are sampled by drilling holes in sample castings from each carload, according to some fixed mathematical routine established at each plant. Sometimes a set of five bars are taken and one hole drilled halfway through each but in different positions. The bars are then turned bottom up and drilled halfway through again so as to bring the holes " staggering," or in reverse order.

In some refineries templets of sheet metal are made to fit each size of casting received. These templet plates are perforated with uniform rows of numbered holes, which are used, one on each pig, in a fixed system of rotation to secure a good average sample of a carload in spite of the marked segregation of precious metals in any individual casting of the copper.

When refined cakes or bars for rolling are to be tested, it is the purity of the clean metal itself that is required, and the surface oxides should be accordingly removed before drilling.

In the case of ingots which are to be placed directly in the pots at the brass foundry, the fairest way to sample a lot is to bore in each of two or three sample ingots six holes ($\frac{5}{16}$-inch diameter)

halfway through from the top and then halfway
from the bottom, including the surface oxides, and
let the mixed drillings constitute the sample.   This
would not hold exactly true, however, in the case
of very deep wedge-shaped ingots in which the
greater part of the weight is contained in the upper
half of the vertical section.

The following tests are now made upon the
finished metal at all large refineries and foundries:
(I) Mechanical, (II) Electrical, (III) Chemical.
The first two are described in a paper presented to
the Lake Superior Mining Institute, and only the
third is considered here.

Practical men often object to the small scale of
laboratory researches.   A valid objection can be
made to some of the figures taken as standards for
the strength, ductility, electrical resistance and
specific gravity of copper.   The values were, in
most cases, deduced from experiments with copper
remelted and cast from crucibles.   Commercial
copper, melted under charcoal, is nearly deoxidized
by the charcoal and does not crystallize like that
refined in reverberatory furnaces.

To eliminate this objection, some determinations
of specific gravity were made from the native mass
copper, the refined product (both cast and rolled)
and metal remelted in contact with charcoal.

Copper deoxidized by melting and cooling under
charcoal in a charcoal cup compares not only in
density but also in the large size of its crystals, as
revealed by the microphotograph, with the native
mass copper direct from the mines.

Assay of Gold and Silver

At the suggestion of Dr. Le Doux the " wet " and " all-fire " methods were discussed by several assayers in the Trans. A. I. M. E. for 1894. A later account of the work at the Mint was given by Whitehead and Ulke. Ulke described the " all-fire " method in the same form in which the writer employs it. Ten samples of 0.1 assay ton are each scorified with 50 grams of lead, and the assays are finally combined into two for final cupellation. Assayers agree that the results are a little higher in gold than by the combination method, which is too well known, also, to need explanation. With any copper fairly free from silica and sulphur much time and chance for error may be saved by cupeling the gold and silver chloride directly without scorification. This short-cut method is in regular use in at least three American refineries.

Estimation of Pure Metallic Copper in Commercial Metal

The principle of electrolysis is the only one to be depended upon. In the titration methods, usually employed for low-grade material, the margin of difference in the case of refined copper between standard and sample is too small, and the liability to appreciable error is too great to permit as exact work as the battery assay. For the electrolytic assay, 4 to 5 grams of metal is the least quantity which will theoretically produce results accurate within a limit of error of 0.01 per cent.

A strong magnet should always be passed through the drillings before weighing. Neglect of this precaution has probably been the cause of some discrepancies in the results of different laboratories.

The electric current for the work can be very easily furnished, where a direct-current system is used for electric lights, by reducing the current with a bank of incandescent lamps. All the lamps are placed parallel with each other, but the whole bank is in series with the electrolytic assays. Where a continuous day current is not available, two sets of storage cells are very convenient, with disk rheostats for regulation.

Copper will deposit better from a solution of dilute sulphuric acid with a little nitric acid than from either acid alone.

In the account of a process recently devised for the direct electrolysis of copper containing traces of antimony and a heavy percentage of arsenic, the saturation of the solution with nitrate of ammonia was recommended. I now find it more convenient to prepare a saturated stock solution of this salt and to proceed as follows: To the solution of 5 grams of the arsenical copper in 20 cc. of nitric acid add 50 cc. of the saturated solution of ammonium nitrate, neutralize the copper solution with ammonia till slightly basic and then add 1.0 cc. of strong sulphuric acid, or enough to make the liquid slightly acid. Fill up with the ammonium nitrate solution until the body of the cylindrical platinum electrode is just covered. Loss from spattering is prevented by split watch glasses. Current $ND_{100} = 0.7$ ampere,

counting both sides of the cathode. As soon as the solution becomes colorless, wash down the cover and the walls of the beaker with a fine jet, and reduce the current to 0.5 ampere ND_{100} = the density in amperes per square centimeter of cathode surface.

The waste solutions can be preserved and the ammonium nitrate recovered by treating the neutralized solution with hydrogen sulphide, evaporating to a jelly and re-solution.

Oxygen. — The estimation of oxygen by solution of the copper in neutral nitrate of silver is an uncertain reaction. The well-known German authority, Dr. Hampe, has developed the most accurate method, that of ignition of the finely divided material in a current of dry, pure hydrogen gas, and the determination of the resulting loss of weight of the metal. Archbutt, Hofmann and others have somewhat shortened and improved the process, doing away with a preliminary heating or drying in carbonic acid gas.

According to personal experience, however, the apparent loss of weight is not all oxygen and must be corrected for any arsenic or sulphur driven off. Any oil is removed from the copper filings (or very fine chips) with pure petroleum ether (completely volatile below 60° C.) or, according to Archbutt, with ethyl ether.

The metal is then carefully dried and transferred to a dried and weighed bulb tube, or to a porcelain crucible, to be enclosed within a Shimer combustion apparatus.

The newer form of apparatus, made by E. H. Sargent & Co., Chicago, is even more convenient for a quick approximate ignition, as the crucible is flanged and clamped, and can be withdrawn without disturbing the tube connections. The air is first driven out by a current of hydrogen, then the bulb tube is heated to a red heat with a flat-flame Bunsen burner for one hour, and cooled in the current of hydrogen. The hydrogen is finally replaced by dry air and the tube weighed. The writer absorbs the hydrogen sulphide evolved in an ammoniacal solution of cadmium salt and weighs the cadmium sulphide formed.

Chemists differ somewhat in the means they employ for the purification of the hydrogen gas. As investigators on atomic weights have recently observed, strong sulphuric acid should not be used as a drying agent, since hydrogen has a slight reducing action upon it.

It is best to purify the gases in separate trains of tubes as follows: Air train: (1) elevated pressure bottle; (2) concentrated sulphuric acid tube; (3) potassium hydroxide solution in absorption bulbs; (4) long, gently inclined tube of concentrated sulphuric acid. Hydrogen train: (1) automatic generator; (2) Liebig tube with saturated solution of mercuric chloride to remove hydrocarbons; (3) potassium hydroxide bulbs; (4) bottle of silver nitrate; (5) large tube filled with fused stick potassium hydroxide cut into small pieces; (6) drying tube of fused, granulated calcium chloride. The air and gas " trains " are led to one three-way glass

stopcock, so that a positive pressure is always maintained at this point.

Beyond the ignition tube is a small bent tube for the partial condensation of water, etc., and another three-way stopcock. One tube from the stopcock leads to a calcium chloride drying tube and hydrogen jet, the other to the bottle of cadmium solution. The objection to the employment of a crucible apparatus, instead of the less convenient bulb tube, lies in the difficulty of saving any volatilized arsenic, lead oxide or sulphur.

Sulphur. — The completeness of removal of this harmful element from the copper of commerce depends on the care with which the final rabbling and poling process is carried out. The best refined copper contains hardly a trace. It is perhaps not sufficiently understood or appreciated that hot copper absorbs both oxygen and sulphurous gases with great avidity when considerably below the melting point in the annealing furnace.

The only rapid and exact method for the estimation of traces of sulphur in the refined product which has appeared in print is one presented by the writer to the American Chemical Society in 1895. This depends on the removal of the copper from its solution in pure nitric acid by electrolysis. The solution, freed from copper, is gradually transferred to a No. 3A casserole and evaporated to dryness over an alcohol flame with the addition of a little sodium carbonate to retain the sulphuric acid. The remaining nitric acid is removed by two evaporations with hydrochloric acid. If any lead sulphate

is found on the filters, they are boiled with a little sodium carbonate to render the sulphuric acid soluble and ready for precipitation by barium chloride. A blank analysis must be performed with the acids and distilled water, which will show usually about 1 mg. of barium sulphate. When the copper contains much sulphur it is necessary to use aqua regia for its solution, and remove the hydrochloric acid by subsequent evaporation with nitric acid.

Other Foreign Metals in Copper. — In the determination of metallic impurities we find among chemists considerable divergence of methods.

When a complete analysis is to be made, the filtrate from the 50 gram assay for gold may be taken for the determination of the arsenic, antimony and tin group, or for selenium and tellurium. Technical chemists, so far as I know, employ some modification of Dr. Hampe's original process for the separation of the bulk of the copper when a complete test is to be made. As routine refinery tests are often only partial, the daily practice is to determine single elements by special tests.

Arsenic, Antimony and Tin. — Arsenic may be determined by (A) the Fischer or Lundin distillation of the copper with ferrous sulphate and hydrochloric acid.

(B) by Aller's method, or distillation of the arsenic in hydrochloric acid solution, using an aliquot part (two-fifths) of the copper to reduce the solution of the remainder. The arsenic is obtained from the distillate, and the material in the flask is then evaporated almost to fusion with 75 cc. of

a saturated solution of zinc chloride to distill off
the antimony. The residue is cooled, treated with
20 cc. of hydrochloric acid and evaporated again.
I have no experience with this scheme.

(C) Heberlein's method removes 98 per cent of
the copper from the refined product (or 90 per cent
from the crude) by electrolysis in a mixture of nitric
and sulphuric acids containing 2.5 grams of ammo-
nium nitrate, as in Hampe's original method. The
solution is then treated with hydrogen sulphide,
the arsenic and antimony separated as sulphides by
sodium sulphide, and dissolved in hydrochloric acid
(2:1) by the aid of a little potassium chlorate.
Hydrochloric acid is added until the solution con-
tains enough to prevent the precipitation of anti-
mony (3 acid: 1 H_2O) and the arsenic precipitated
by hydrogen sulphide. The liquid, after filtration,
is diluted to four times its original bulk so that the
antimony may be precipitated.

(D) The Baltimore method for arsenic and anti-
mony depends on the separation of impurities by
precipitation with ferric sulphate and excess of
ammonia. This principle was said to be due to
Lehman, Mager and Johns, and was also used by
Keller.

I perform this separation as follows: Fifty grams
of clean copper are dissolved in 200 cc. of strong
nitric acid and diluted to 1 liter. If the metal is
known to contain less than 0.05 per cent arsenic,
add 1.5 grams of crystallized ferrous sulphate
($FeSO_4 + 7 H_2O$), or about 1 gram of the anhydrous
$FeSO_4$. If the material is rich in arsenic, use 2.5

grams of the crystals. Heat the solution to boiling and add strong ammonia until basic salts of copper are redissolved. If antimony and bismuth are to be determined, add (as soon as the ferric hydroxide is down) 0.75 gram of ammonium carbonate and a few cubic centimeters of a standard solution of sodium phosphate. After three minutes' boiling and ten minutes' settling in a warm place, pour through a 15-cm. filter, keeping the solution hot to prevent crystallization. Wash two or three times with dilute ammonia (1:20), wash the precipitate back into the beaker and clean the paper with a little dilute sulphuric acid, finally treating it with dilute ammonia. Dissolve the iron completely, reprecipitate, filter and wash as before. Finally redissolve in dilute sulphuric acid and pass hydrogen sulphide gas, filter and extract the arsenic group with a little hot dilute sodium sulphide (sp. gr. 1.1).

(E) This method consists in separating the arsenic from the copper by method (D) or (F) and then precipitating the arsenic with neutral silver nitrate from a solution of the arsenate, made neutral (according to the recommendation of Canby) with a slight, but permanent, excess of an emulsion of zinc oxide. To oxidize a minute amount of arsenic the ferric hydroxide precipitate is ignited, weighed, ground in an agate mortar to an impalpable powder, the remainder reweighed and fused with 8 parts of a mixture of sodium carbonate and potassium nitrate. If the arsenic is over 0.05 per cent, precipitation of sulphide is safer than any attempt at fusion.

By experiment with the process, as described, using pure arsenic, results below the theory were obtained. By precipitating the arsenate of silver, however, in presence of an excess of suspended zinc oxide, stirring vigorously for five minutes to insure complete neutralization of the nitric acid set free by the reaction, the results have been more satisfactory. 25.0 parts of arsenic correspond to 107.93 parts of silver.

(F) The alternative method of Dr. Hampe, which involves the saturation of the sulphuric acid solution of the copper with sulphurous acid gas and the precipitation of the copper as cuprous sulphocyanate, is accurate, but requires considerable personal attention and tedious manipulation.

If there is much antimony with the arsenic, Heberlein's scheme of precipitation by hydrogen sulphide in strong hydrochloric acid solution is the best for the subsequent separation of the two elements.

I do not think it safe to assume that the copper in crude material can be separated completely from the arsenic and antimony by electrolysis, unless a set of conditions which have been proved by experiment to give perfect results are rigidly adhered to. A large amount of ammonium nitrate will lessen or prevent trouble.

(G) The writer makes use of all the methods outlined, giving preference for accurate work to the precipitation with sulphate of iron and ammonia. ·The antimony and arsenic are separated and the arsenic oxidized to arsenic acid for the final precipitation (a) by fusing the ferric hydroxide

precipitate or (b) by filtering the sulphide on an asbestos felt and dissolving the dry arsenious sulphide in red fuming nitric acid. This acid must be full strength or the arsenic will not be completely oxidized. The solution is filtered and evaporated on the water bath with the addition of 0.1 gram of sodium carbonate.

Where much arsenic is present I find that the arsenious sulphide is very apt to retain sulphur, even when precipitated in the cold and carefully extracted with absolute alcohol and carbon disulphide, and the sulphide should be redissolved and determined (a) as arsenate of silver in the neutral solution of the nitrate, as described above under (E), (b) by precipitation as magnesium ammonium arsenate in a solution of very small bulk. The solution of purified arsenic acid in nitric acid having been evaporated to dryness, the residue is treated with 0.5 cc. of hydrochloric acid, 5 cc. of water and 0.1 gram of tartaric acid. The solution is filtered, the filter washed with a very little water made alkaline with ammonia and made up to 10 cc. in volume. It is then, cooled, 3 cc. of magnesia mixture (Fresenius's formula) and 7 cc. of strong ammonia added and the solution stirred for five minutes and allowed to settle overnight.

The foregoing details apply to the precipitate obtained from a 50-gram sample of metal containing less than 0.1 per cent of arsenic. If richer than this percentage, increase the volume of solution and the reagents one-half. Always test the filtrate for complete precipitation. Dry the precipitate and

carefully char the small filter separately by repeated gentle heat and moistening with a saturated acid solution of ammonium nitrate.

If tin is present, it may be separated from antimony by a modification of F. W. Clark's method of precipitation by hydrogen sulphide gas in a hot solution saturated with oxalic acid. The volume of the solution should not be over 25 to 50 cc.

Antimony sulphide is ignited in a porcelain crucible to the tetroxide.

Selenium and Tellurium. — These elements are usually determined in a separate sample by the method of Edward Keller. The impurities are separated by precipitation with ferric hydroxide, which must be in large excess, and the selenium and tellurium are finally precipitated from a hydrochloric acid solution with sulphurous acid gas. Where a separation of the two is not desired, it is quicker and more convenient to precipitate them by stannous chloride. It is most accurate to filter and dry the selenium or tellurium on thin felts of the best asbestos and, after weighing them, to ignite and determine the elements by loss as a check. Dr. H. F. Keller has recommended hydroxylamine as a precipitant.

Lead, Iron, Zinc, Nickel and Cobalt. — The bulk of the copper is removed by electrolysis and any deposit of lead peroxide on the anode is weighed. Fifty grams of copper are dissolved by a mixture of 50 cc. strong nitric acid, 80 cc. of sulphuric acid and 400 cc. of water. The solution is diluted with 600 cc. of water and the copper is precipitated on a

large platinum cylinder, which may, with advantage, be perforated with narrow slits, as recommended by Heberlein. With a fixed anode the copper is deposited in about twenty hours, using a cathode 11×11 cm. and a current of 3 amperes. With a rotating anode (at 600 to 1000 revolutions per minute) the copper can be deposited in nine hours.

The following design for a rotating anode has been found satisfactory for use with platinum cylinders. A straight, stiff wire is bent back and forth at one end. A disk the size of a quarter of a dollar is cut from a sheet and is slit on radial lines to form ten propeller blades, and a small hole bored in the center through which the bent end of the wire is passed and clamped by pressure. This is revolved to generate downward pressure, which takes the weight off the spindle and greatly lessens the friction.

When the copper is deposited the solution is concentrated, transferred gradually to a small casserole and evaporated to fumes to remove the free sulphuric acid and most of the ammonium salts. The residue is dissolved in water and any lead sulphate and silica are filtered off and saved. Hydrogen sulphide is then passed through the acid solution, the precipitate filtered off and washed with hydrogen sulphide. The precipitate is extracted with a little dilute hot sodium sulphide and the residue is combined with the other precipitates containing lead for the separation of that element as sulphate.

The main solution (volume = 30 to 50 cc.) is oxidized and the iron precipitated with ammonia.

The filtrate is acidified with acetic acid and one-fifth its volume of glacial acetic acid added. The zinc is then precipitated in the cold by hydrogen sulphide, and ignited and weighed as oxide. A trace of lead may make its appearance here. Formic acid (sp. gr. 1.2) is even better than acetic acid.

After removal of the acetic acid by evaporation, or, if this is not convenient, after neutralization, the solution is heated to boiling and the cobalt and nickel precipitated by hydrogen sulphide.

The cobalt and nickel are separated in a small volume of solution by the potassium nitrite method, and after resolution in sulphuric acid the metals are deposited from an ammoniacal solution by electrolysis.

Manganese. — This element is rarely present in refined copper. It would appear on the anode during electrolysis and could be weighed.

Bismuth. — A trace of this element is generally determined by a special method unless it has been separated with the arsenic and antimony by precipitation with ferric hydroxide. It is usually estimated by adding excess of ammonia and some ammonium carbonate to the solution of 50 grams of metal and boiling. A little iron should be present. The precipitate is filtered off and purified from copper by repeated precipitation. The bismuth is then thrown down as sulphide, and may be purified from a trace of copper by the well-known treatment with a little potassium cyanide. It can finally be weighed as oxide, or estimated by a color test

To secure accurate and trustworthy results in

copper analysis it is necessary not only to be very careful in manipulation but also to carry through blank analyses with all the reagents.

Even the distilled water will frequently show a trace of tin derived from the still in which it was condensed.

THE EXACT ELECTROLYTIC ASSAY OF REFINED COPPER.[1]

1. Details of Standard Slow Method. — A 5-gram sample has been adopted by ourselves and at several other plants, because it eliminates errors of sampling the bottled drillings in the case of refined metal, and is the largest amount of material which can be started at close of business and taken off and weighed the next day before dinner time without oxidation from too large a current.

Assays must finish, under the conditions described, in 16 to 18 hours, and without any more than a trace of preliminary gassing at the cathode, or be rejected.

This theorem goes farther than the requirement of other laboratories, but has been proved that we can thus absolutely prevent an occasional oxidation, or absorption of hydrogen, which cannot be detected by any marked change in color, but which may amount to 0.02 per cent by weight.

The assays are started with a current whose normal density, counting both sides of the cathode, is 1 ampere per sq. cm., and in the morning, as soon

[1] George L. Heath, J. Ind. Eng. Chem. Vol. 3, No. 2, 1911.

as the liquid is colorless, the split watch glasses covering the beaker are washed down with a fine jet, and the current reduced to 0.5 ampere.   If assays have to go more than 18 hours and the cathode shows bubbles of gas, the current is cut to 0.25 ampere to avoid oxidation or hydrogen absorption.

The sample is weighed into a lipless beaker about $4\frac{7}{8}$ inches high and $2\frac{1}{4}$ inches in diameter outside, across the bottom, and of 300 cc. capacity, which can be obtained from Eimer & Amend, New York.

In the slow method, chemists use the foil, plain or corrugated.   The cylinder is 2 inches (or 5 cm.) high and the closed cylinder has a total surface of 150 sq. cm.   The cylinder, opened on one side, which the writer prefers for the ease and quickness with which it may be withdrawn from the solution and dropped into a beaker of water, is 100 sq. cm., counting both sides, and the stem extends 12.5 cm. above the cylinder.

The sample of drillings is heated on a steam plate, just below the boiling point, with a mixture of exactly 7 cc. of C. P. nitric acid (sp. gr. 1.42), 10 cc. of sulphuric acid (sp. gr. 1.84) and 25 cc. of distilled water, with the beaker tightly covered until solution is complete, as can best be determined by holding the beaker over a white paper.

The solution is brought to a total volume of 120 cc. before electrolysis.   When the deposition is thought to be complete, 1 cc. of liquid is withdrawn with a glass medicine dropper, placed in the cavity of a white porcelain tile, and treated with a few drops of freshly prepared hydrogen sulphide water.

Any copper over 0.000005 gram will show at once, and is easily distinguished from the yellow of arsenic which would show later.

After years of experiment, we have found that the proportion of acids given produces exactly the right equilibrium of the acid ions in the solution at the completion of the assay, preventing the deposition of the arsenic if the amount of total acid is increased with the arsenic.

In practice, some works, like ourselves, make up a dilute acid, mixed " Stock Solution," and run it from a large burette.

For 5 grams metal, containing less than 0.03 per cent arsenic, the " Stock Solution " required would be 40 cc.; 0.03 per cent to 0.100 per cent arsenic, 50 cc.; for 0.11 per cent to 0.500 per cent arsenic, 60 cc.

It is found to facilitate the instantaneous removal and washing of the cathode without loss, if the beakers are arranged in a row under a vulcanite plate $\frac{1}{4}$ inch thick and perforated with one small hole for each wire stem to make connection with the split, brass terminals (which rest in pairs about $1\frac{5}{8}$ inch apart from center to center) and are perfectly protected by the plate from acid fumes.

The under side of this strip, or shelf, is $12\frac{1}{2}$ inches from the table, and the beakers stand on double-headed, turned wooden spools, 6 inches high.　When any assay is finished, the spool can be slipped aside, and with one motion the beaker can be lowered, and a beaker of distilled water raised to cover the electrode and remove acid before it is disconnected.

The cathode is then washed well with a jet, the water removed by pouring a lot of clear 94 per cent alcohol over the plate, and the little that remains after draining a moment is then burned off and the plate carefully passed across the flame of the lamp to be sure that no trace of liquid remains between the stem and the cylinder.

The electrodes are cleaned, heated, and weighed before use, allowing the same length of time for cooling before weighing, and the weights should be compared very carefully and regularly with a standard set.

The foregoing claims for the deposition of pure copper, with either the slow method or the " rotary," do not strictly apply to copper containing more than a trace of antimony, selenium or tellurium, in which special methods of preliminary purification of electrolyte are employed,[1] or a " dope " may sometimes be used as recommended by the chemists of one of the Tennessee copper companies.[2]

To relieve any doubt as to the purity of the copper deposits, in the case of material carrying over 0.1 per cent arsenic, the cathode can be redissolved without loss by placing the cathode copper in 40 cc. of acid " Stock Solution " dilute to 120 cc. with water, allowing it to stand on the steam plate just below boiling for about an hour.

The beaker must be carefully covered with a

[1] Trans. A. I. M. E., 27, 390, 1897; J. Am. Chem. Soc., 26, 1120, 1904.

[2] Eng. and Min. J., 89, 1910.

glass cover perforated near one edge with a small drilled hole just large enough to pass the stem of the electrode. If any assay was allowed to boil, any steam which raised the cover would cause a certain loss of copper solution by spraying.

Check results should agree within 0.01 per cent.

It will be noted that, whereas Mr. Ferguson recommends the previous removal of silver from converter metal when aliquot portions of a large sample are volumetrically taken, we find it better with standard refined metal to deposit the silver with the copper, and determine silver by a special assay if required, since weighing, even with the elaborate precautions sometimes adopted, is more accurate than measuring.

In the case of refined copper, we must also have an absolute test of the completion of the deposition, which is obtained by taking out 1 cc. of the electrolyte, when the assay is thought to be finished, by means of a glass medicine dropper, and treating it on a white porcelain tile with a few drops of freshly prepared water solution of hydrogen sulphide.

If the estimation of the arsenic is desired, the electrolyte from a 5- or a 10-gram assay can be used for the purpose, with certain precautions to be described in a paper on the estimation of the arsenic group.

Some works find the 110-volt direct lighting current to be the most satisfactory source of electric power, which is reduced by small rheostats in series with each group of 5 or 6 assays, or by a bank of

incandescent lamp sockets, into which lamps of different candle power can be inserted to vary the current.

Where the current is alternating, recourse is had to small " motor-generator " sets, rectifiers, for the purpose of charging large storage batteries, which give a much steadier current than very small machines.

2. Rapid Assay by the Rotation of the Electrolyte. — Rotation in a magnetic field offers great possibilities for special rapid work where results are desired at once on copper or slags containing arsenic and antimony. The principle has been somewhat discussed and so a description of the simple design we have adopted will be given.

There are two or three elaborate forms of these solenoids on the market already, one being made in Detroit, which have arrangements for raising and lowering both electrodes, and are mounted in pairs on a small marble slab.

The pattern we use has been made in two sizes: the first to accommodate the battery assay beaker described, and a very large size, which will take a 500-cc. or even 750-cc. beaker, for the removal of larger quantities of copper, up to 50 grams, in a complete analysis of the metal. The best results have (Figure 16) been obtained by winding 500 turns of No. 13 B. & S. gauge magnet wire upon a copper cylinder of a diameter a little larger than the top of the beaker, as specified in the sketch, and made of metal $\frac{3}{32}$-inch thick.

The cylinder is brazed to a water-tight joint, at

the top and bottom, to thin plates of soft $\frac{3}{32}$-inch steel, which complete the spool holding the coil of wire.

At first a thin shell was placed around the outside of coil after winding, to prevent magnetic leakage, but it was found that this confined the heat too much, and was not necessary.

A hole is bored in the upper steel plate, of a size equal to the inner diameter of the cylinder, and a
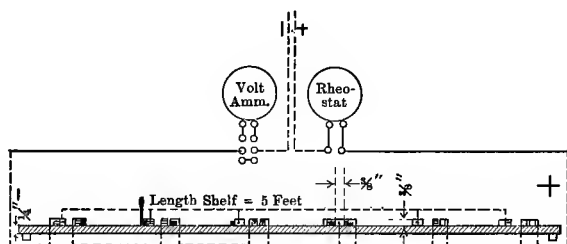
Fig. 16.

1-inch hole through the bottom plate for ventilation or for the insertion of a stopper and glass tubes for water cooling.

It is necessary to complete success with the rapid method to make use of a gauze cathode, weighing 16 to 17 grams, made of gauze measuring about 17 meshes to the linear centimeter or 40 meshes to the linear inch, and wire-bound for strength.

A closed cylinder to fit inside the beaker loosely would have an area, counting both sides, of 150 sq. cm., but for the ease and quickness with which it may be withdrawn from the solution, the writer

prefers the cheaper form, open on one side, having a total surface of 100 sq. cm.

The copper is prepared for electrolysis exactly the same as in the standard method, but there is a limit to the amount of acid " Stock Solution " which can be used.

If over 50 cc. are present in the 5-gram assay, the heat and strong current will finally cause the metal to redissolve from the cathode.

When the test is finished, as shown by the hydrogen sulphide test, the electrode is quickly withdrawn, or the liquid is siphoned out while a stream of fresh water is allowed to flow in.

The wire coil may be in series with the assay, or a set of wire coils in series with each other may have a current sent through them from an independent switch.

We find it advisable to use about the same amperage in the assay as in the coil, and a current N density on 100 sq. cm. = 6 amperes will complete the deposition of 5 grams of metal in two hours, the amperage being cut, however, to 2 amperes as soon as the solution becomes colorless and the cathode shows a little polarization, which requires about 70 minutes.

The writer prefers, nevertheless, to employ only $4\frac{1}{2}$ amperes, as there is not so much heating and oxidation effect, and the same current can be maintained throughout, completing the assay in $2\frac{1}{2}$ hours.

The double pair of split watch glasses used for a tight cover are washed down as soon as the solu-

tion is colorless, and in about half an hour thereafter a test is made of the solution.

According to theory, $6\frac{1}{2}$ amperes would deposit the metal in about 39 minutes, but the removal of the last traces requires a long time.

The assay must be sharply watched, and the cathode removed as soon as the last trace of copper is out, or a difference of a few minutes may permit a slight oxidation of the deposit.

In very accurate work on extremely arsenical metal, the cathode can be redissolved, with the precautions to avoid loss by spraying described in the first method, and the deposition repeated in the fresh acid solution (Figure 17). A trace of platinum will appear in the solution on dissolving the cathode in dilute mixture, and can be filtered out and deducted if desired.

This trace of platinum would interfere with the direct estimation of traces of arsenic in the copper-free electrolyte, unless removed.

Rotary Apparatus has been Made in Two Patterns. — Some prefer to make the frame 12.5 cm. (= 5 inches) high and 12.5 cm. in diameter, but the dimensions in Figure 17 permit a better inspection of the liquid and concentrate the effect on the lower half of the beaker. A small glass overflow tube, as shown, will permit the regulation of the heat, but water circulation should not be employed in the regular battery assay with small apparatus, as the heat, if not too near the boiling point, is one factor in holding the arsenic in solution.

Rapid Assay of Copper in Furnace Slags. — Thorn Smith and others have improved the methods of assay of reverberatory and waste cupola slags containing such a large amount of iron that the old ammonia precipitation (Heine's blue test) will not yield all the copper.
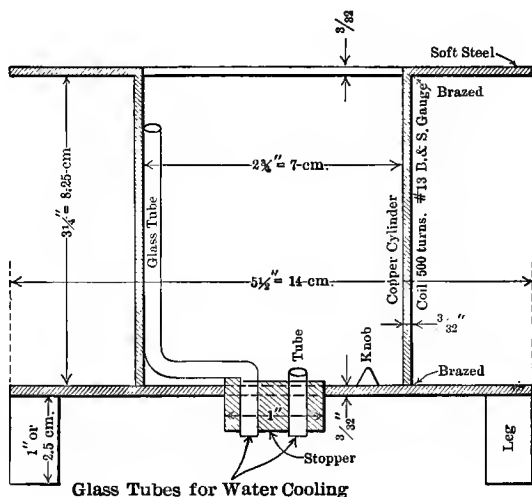
Fig. 17.

The rapid electrolysis by rotating anode or by the solenoid is far preferable, and the latter device is the better of the two, as we use it.

Two and five-tenths grams of waste slag, or 1 to 2 grams of richer slag or ore, are weighed and placed in a No. 4 porcelain casserole, moistened and treated with 15 cc. of strong nitric acid and

boiled one minute to decompose it, but not long enough to burn on the bottom.

Most slags decompose well if the slag has been chilled by granulating in water at the furnace. Then add 10 cc. of concentrated sulphuric acid and boil to dryness over a gauze, but stop just before the sulphuric acid begins to fume. This allows a trace of nitric acid to remain, and in presence of excess of iron produces a good deposit in the rotating solution in 30 minutes, with a current whose strength is N density 100 sq. cm. $= 4\frac{1}{2}$ amperes, counting both sides of the cathode.

The assay must be watched and split electrode of foil removed promptly.

The gauze cathode will not be necessary except for rich slags requiring over 30 minutes. The residue in the casserole is treated with water while still hot, and washed directly into a regulation beaker, without filtration.

Chilled waste slags, which are low in iron oxide and high in lime, can sometimes be decomposed in a few minutes with a simple boiling in the tall beaker in 60 cc. of " Acid Stock Solution " and then transferred to the solenoid. Sometimes, as metallurgical chemists find out to their cost, special slags require an aqua regia treatment and fusion of the residue.

THE DETERMINATION OF ARSENIC AND ANTIMONY IN COPPER

This paper will summarize the principal methods employed in American foundries and refineries, and include a new rapid method for arsenical metal by

direct titration of the electrolyte from battery assays or by titration of a solution of precipitated sulphides of the arsenic group.

The principle of separation of arsenic and antimony from copper is either distillation or gravimetric separation.

Distillation. — Two of the largest laboratories in the United States use some form of this method.

If it is desired to estimate the antimony, as well, by evolution, a mixture made something like the following is used as a distilling solution for decomposition of the sulphides of the arsenic group, which are washed into the still with a little strong hydrochloric acid, completing the extraction from the paper with a few cubic centimeters of sodium sulphide solution, or the sulphides can be filtered on a felt which is transferred directly.

A. Dissolve 150 grams of C.P. zinc in 140 cc. of hydrochloric acid (sp. gr. 1.2) and 440 cc. of distilled water, evaporate until the bulk is reduced to about 370 cc. Mix this solution with the solution of 100 grams of C. P. cupric chloride, dissolve in 330 cc. of concentrated hydrochloric acid. The total volume of mixed solution = 700 cc.

For slags, etc., take 30 cc., for refined copper 75 cc. of the solution, distill down in the flask which is connected with a short vertical glass condenser, until a thermometer in the neck of the flask shows 120° C., then add 35 to 40 cc. additional acid liquid and distill again. The condenser dips under water in a No. 3 or No. 4 beaker, and the distillate is

finally removed and titrated with iodine as shown later under the " titration of arsenic."

A clean beaker of water is then placed below the condenser and the attempt is made, I understand, at two laboratories, to recover antimony by a further distillation at 122° to 160° C.

The antimony may be separated gravimetrically by separating its sulphide from the copper by extraction with dilute sodium sulphide solution (sp. gr. 1.08) and from the trace of tin, which is due to reagents and distilled water, by repeated precipitation and filtration in small volume (25 to 50 cc.) of concentrated oxalic acid.

B. The iron precipitate obtained as described under method C is washed into the Allihn flask by 100 cc. of strong hydrochloric acid, and then neatly reduced with about 5 cc. of 50 per cent hypophosphorous acid, and distilled at a temperature below 120° C. The condenser dips under water in a No. 3 beaker, and the distillation is repeated with 50 cc. more of the acid. In the writer's opinion, a third distillation should then be made into a beaker of fresh water, which is separately titrated, and the process continued until the distillate shows no more traces of arsenic than one can always expect from the best acid.

Fifty cc. of concentrated zinc chloride solution are then added (W. H. Bassett's method) and the distillation continued at a temperature above 122° C. to evolve the antimony.

In the writer's experience, this distillation process is uncertain and requires repeated treatments

to be sufficiently accurate for refined metal.   The following gravimetric methods, accordingly, are to be preferred:

C. Gravimetrically, by separation with large excess of iron salts and ammonia.   Place the clean weighed copper drillings in a beaker, and dissolve on a steam plate in strong nitric acid (sp. gr. 1.42).

For refined copper, containing less than 0.03 per cent arsenic, we take 50 grams of copper, and treat with 210 cc. of acid, in a No. 7 beaker, but in the case of more impure material it is sufficient to take 25 grams, or less, and treat in a No. 5 beaker (capacity 500 cc.) with 110 cc. of acid.

Dilute with water until the beaker is nearly half full, and add to each assay a solution of 2 grams of C. P. crystallized ferrous sulphate which has been oxidized in a small beaker by heating with excess of nitric acid.

Heat nearly to boiling and add strong ammonia until the iron is precipitated and the copper salts are redissolved.

Fifty grams of metal will require about 300 cc. of ammonia.   Heat to boiling, settle one-half hour on steam plate, and filter quickly through a 15-cm. washed filter supported by a platinum cone with coarse perforations.   It is necessary to keep the solutions warm to prevent crystallization, and the blue color is washed out of the filter with water made slightly alkaline (1 NH_4OH : 10 H_2O).

If the bismuth is to be determined with antimony, add 2 grams of ammonium carbonate and 5 cc. of saturated sodium phosphate solution to the

solution as soon as the iron is precipitated as hydrate.

When the sample contains less than 0.0100 per cent arsenic + antimony, the filtrate is passed through a second filter, to recover any traces of iron mechanically lost in the first washing.

If the copper is more impure than the above limit, make the blue filtrate acid with nitric acid, add 0.500 gram of the oxidized ferrous sulphate, and precipitate and filter again to clear the solution.

Redissolve the large precipitate in dilute sulphuric acid, treat the filter paper with a little ammonia, precipitate again, and pass through the same filter. If a second iron precipitation was made, dissolve this small amount of iron, add it to the blue filtrate from the last treatment of the major precipitate, add excess of ammonia and filter on a small filter.

Combine the two precipitates, dissolving them in hot dilute sulphuric acid containing 5 per cent by volume of hydrochloric acid, and throw down the arsenic, etc., with the last traces of copper, by 15 minutes' cold treatment with a stream of hydrogen sulphide.

Allow to stand until granular and well settled, then, before night, charge again with the gas and allow to settle overnight.

In the morning, pass gas again until the solution smells strongly and filter on a 7-cm. filter, then wash the beaker and tube by rubbing with bits of filter paper. Transfer paper and contents to a small No. 0 beaker.

By the double gas treatment before filtering, the arsenic is generally brought down with the copper, instead of after it, but the filtrate should be charged with gas again and allowed to stand until settled, and the operation repeated until precipitation is complete.   We dissolve the sulphides of arsenic and antimony with traces of tin by hot digestion with sodium sulphide, using as little as possible, and washing, by stirring and pressure, with slightly alkaline hydrogen sulphide water.   Heat and filter again if any copper goes through, add 0.2 gram solid sodium hydrate or potassium hydrate, and evaporate to dryness on the steam plate, then treat the residue with about 20 cc. of the strongest fuming nitric acid, and digest until the sulphur is dissolved.

The method of oxidation of sulphides with hot hydrochloric acid and potassium chlorate sometimes involves a loss of arsenic.

Remove the cover from the beaker, if the arsenic is to be subsequently weighed, and evaporate to dryness again.

If the arsenic is to be separated from the other elements, the following method used in Montana is found to be superior to distillation.

Dissolve the dry residue in 25 to 50 cc. of hydrochloric acid (2 parts of acid (sp. gr. 1.2) and 1 of water), adding a small crystal of tartaric acid. Precipitate the arsenic from a cold solution with hydrogen sulphide, allow to settle for a short time, filter on an asbestos felt, and wash with acid of the same strength.

As soon as the filtrate is washed out and the sulphide wiped from the beaker with a little asbestos, the filtrate can be removed and the acid removed from the felt with some H_2S water.

Test the acid solution again and if no more arsenic appears throw down the antimony and traces of tin and copper with H_2S gas.

Selenium or tellurium, if present in sufficient quantity to interfere, may be removed by reducing the HCl solution with sodium sulphite or SO_2 gas before the H_2S treatment. Hydroxylamine can be used to better advantage than SO_2 gas in dilute HCl (1:2) for preliminary separation of selenium plus tellurium from arsenic, etc.

It has been observed that distilled water, unless condensed in iron or glass, as also the ammonia and HCl, generally show a trace of tin, and a blank test of the acids reveals a trace of arsenic but rarely antimony. The felt, with the sulphides, is placed in a small beaker, the sulphur dissolved by digestion on the steam plate with red fuming nitric acid, the solution diluted with one and one-half parts of water, the asbestos filtered out, and the solution evaporated to dryness on the steam plate with 0.1 to 0.5 gram of sodium nitrate, according to the amount of arsenic present, if the latter is to be weighed as magnesium pyroarsenate.

Dissolve the residue in 5 cc. of cold water, with the addition of 10 drops of HCl and 0.1 gram of tartaric acid.

Filter through a $2\frac{1}{2}$-cm. filter into a 25-cc. beaker,

unless the arsenic is known to be over 0.05 gram, and wash with as little water as possible from a fine jet. Make slightly alkaline with ammonia, when the liquid should be clear and not have a volume of more than 11 cc.

Add 3 cc. of magnesia mixture, make up to 20 cc. with strong ammonia and stir 5 minutes. If the arsenic is excessive, increase the precipitant and dilute with ammonia so that the total volume shall be 25 to 30 cc., of which one-third is free ammonia water.

Allow to stand overnight in a cool place, filter on a $2\frac{1}{2}$ or 3 cm. filter, aiding the transfer of the arsenic by the filtrate.

Wash with a fine jet of ammonia (1 to 3 of water) until free from chlorine, dry in an oven, remove the salt to a glazed paper, and place the filter in a porcelain crucible.

Add a few drops of acid ammonium nitrate solution (saturated), char carefully, and repeat treatment until the paper is consumed without a perceptible odor of arsenic.

Transfer the remainder of the precipitate and ignite at a full red heat over the Bunsen burner to a constant weight. The Mg mixture, Fresenius's formula, is as follows: 1 part of magnesium sulphate crystals, 4 parts of ammonium chloride, 8 parts of water and 4 parts of concentrated ammonia (sp. gr. 0.90). The Mg should be free from lime and the mixture should not be used after it has attacked the bottle and dissolved glass from its interior.

Copper Free from Antimony

D. Dr. Hampe, the German pioneer in accurate copper analysis, invented the method involving the reduction of the solution of copper by sulphurous acid gas with the removal of selenium and tellurium, and the subsequent precipitation of the copper as the white sulphocyanate. Dr. H. F. Keller has given a good account of this familiar but somewhat tedious method, and the reader is referred to his paper for details.[1]

Lake Superior metal, not electrolyzed, rarely contains antimony, hence it is not necessary to make the separation in (2:1) HCl if water free from tin is used or the arsenic is to be titrated instead of weighed.

New Volumetric and Electrolytic Method

E. This scheme of direct titration of an electrolyte is believed to be a new one, and will be found to permit much more rapid work with all classes of material containing little antimony, and can also be used with any copper by preparing the solution for electrolysis, separating the antimony and tin, if present, by methods previously published.

Such a method is adapted to routine control of impure material and was developed for the assay of a large tonnage of Lake copper, now produced, which runs high in arsenic but has almost no antimony.

First Modification for Copper with Less than 0.01 Per Cent of Arsenic; without Antimony. — Dissolve

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[1] J. Am. Chem. Soc., 16, 784, 1894.

the metal and separate the arsenic group as in method C, or perhaps D, but omit the final precipitation with hydrogen sulphide gas in (2 : 1) hydrochloric acid, as a trace of tin does not affect iodine in titration. In the rare case in which a trace of gold or platinum is present, the copper can be originally dissolved according to the method just devised by the writer.

Weigh 1 assay ton of very fine drillings (taken with a $\frac{1}{4}$-inch drill) into a No. 4 casserole, add 25 to 30 grams of C. P. solid potassium bisulphate and 100 c.c of concentrated C. P. sulphuric acid, cover, and boil carefully on a gauze, or plate, for 10 minutes, when the metal should be practically dissolved.

Decant acid, without diluting much if possible, and boil any little residue with a little more acid, mix, then dilute, settle, and filter out gold and platinum. If selenium or tellurium is present, it can be reduced from the hydrochloric acid solution of the residue, obtained by evaporation of the first sodium sulphide solution of the arsenic group with fuming nitric acid. Treatment with sodium sulphite will effect reduction, or hydroxylamine, as recommended by Dr. H. F. Keller.

The titration of an electrolyte gives a little too high results on arsenic, when the arsenic is less than 0.01 per cent, because of the presence of a minute trace of platinum which may be found in the electrolyte, and in much of the cathode copper produced in the laboratory by the regular 5-gram battery assay of refined copper.

Whether it has been found necessary to purify the arsenic sulphide from traces of Sb, Pt and Se or not, the residue from evaporation of the sulphide with fuming nitric acid and excess of soda is taken up with sulphuric acid, or better, 25 cc. of strong sulphuric acid are added to the nitric acid solution of the arsenic as soon as the sulphur has disappeared. Instead of a little sodium nitrate, which was recommended in the gravimetric method to hold the arsenic, we add 3 grams of solid potassium bisulphate free from chlorides. This is adapted from Low's method for ores.[1] Heat rapidly on a hot plate until the sulphuric acid fumes for five minutes.

Cool, wash into a 300 cc., long-necked Kjeldahl flask of Jena glass, place in an inclined position on a lamp stand over a small flame, boil off the water, fume 5 minutes again, and when the time is nearly up, flash the neck of the flask with a lamp flame long enough to drive out any condensed liquid from the neck.

This double fuming process, and removal thereby of the last trace of nitric acid, is the secret of success with the process, as in the iodide method for titration of copper.

After the flask has cooled a little, add from a paper 0.5 gram of solid tartaric acid and, giving the flask a whirling motion occasionally, digest until the solution is colorless. Allow to cool, wash into a No. 3 beaker in which a little water has been placed, and fill the beaker about half full.

[1] "Techinal Methods of Ore Analysis," q. v.

One advantage of this scheme is that a dozen digestions can be carried through as easily as one. Drop a small piece of litmus paper into the beaker, add ammonia until the liquid is just alkaline and bring back to the acid condition with dilute sulphuric acid, adding only one drop in excess.

Place the beakers in a large pan of water to cool, when they will be ready for titration with iodine.

This titration will be taken up after the description of the second electrolytic process.

E. 2d part. *Electrolysis followed by direct reduction and titration.* This is the quickest of all methods for control work, and is accurate for any copper containing more than 0.01 per cent of arsenic and no more than a trace of antimony, but the latter if present would have to be removed unless it was permissible to neglect its influence.

If the metal contains less than 0.01 per cent of arsenic, we take two portions of 10 grams of drillings and place them in the beakers used for the usual battery assay of copper, as described in the first paper.

Dissolve in a slight excess of strong nitric acid (sp. gr. 1.42), add 17 cc. of strong sulphuric acid and evaporate to dryness.

A whole set may, of course, be started at once, and when dry and the residue smells sweet, add 12 cc. of nitric acid, and water sufficient to cover the electrode, which has the usual dimensions for copper assaying, about 100 sq. cm., counting both sides of the plate.

Pass a current of N density = 1 ampere until

colorless, then reduce to one-half an ampere; in short, perform the regular electrolytic assay for refined copper, just as described in the writer's first paper.

The small portion of liquid removed for test is washed into a little beaker, treated with a small crystal of potassium bisulphate, or sodium nitrate, and a few drops of sulphuric acid and evaporated until the sulphur is gone, when it is transferred to the main solution now free from copper, which is treated with 3 grams of the solid potassium bisulphate and evaporated until the nitric acid is all driven off and the sulphuric acid has fumed strongly for 5 minutes.

The solution is then washed into a Kjeldahl flask and digested, as already described. In very accurate analyses the first copper cathode is redissolved in 40 cc. of " Stock Solution," as described in the paper on the electrolytic assay, and the copper again deposited and the second electrolyte boiled down with the first.

The " Stock Solution " mixture of dilute acids is not employed for the original solution of the drillings because it is necessary to oxidize all the arsenic to the condition of arsenic acid, or there appears to be some loss — due to the electric current.

If the metal has more than 0.1 per cent of arsenic, two 5-gram assays are taken, using 15 cc. of sulphuric acid and a final addition of 10 cc. of nitric acid for each. If 0.2 per cent of arsenic is known to be present, each of the assays is boiled down, reduced and titrated separately; or if the arsenic

is less, they may be combined as one and boiled together.

If the arsenic is between 0.01 per cent and 0.05 per cent, two 10-gram assays are combined. The remarks on replating apply here.

A blank should be made with each new lot of acids, and digested. If selenium or tellurium is present, we dilute the dry residue of copper sulphate with water and reduce this element with excess of sodium sulphite free from chlorine, or with a rapid current of sulphurous acid gas at a temperature of 40° C., filter and allow to settle, before adding the nitric acid.

Notes on the titration of arsenious acid by iodine follow.

If very rapid work is necessary, the solution can be electrolyzed for the removal of copper in the rotary device, if water-cooled, but more traces of platinum are introduced into the electrolyte and affect the iodine in titration.

In presence of antimony the electrolyte can be boiled down until the nitric acid is off, then diluted with one and one-half volumes of water, strong hydrochloric acid added in amount equal to the total and the arsenic separated by treatment of the cold liquid with excess of hydrogen sulphide.

Even with this modification this method is more rapid than the gravimetric or distillation, particularly as a number may be done at once, in conjunction with regular copper determinations.

A few words may be of interest in the description of a large rotary device which is of great assistance

in removing the copper from solutions of either 25 or 50 grams of metal, in order that the electrolyte may be evaporated down to small bulk for the estimation of iron, zinc, nickel, cobalt, lead, etc., and, with an extra precaution to separate a trace of platinum, may be used to determine arsenic.

Dimensions: Size of beaker, No. 4 and 5 low form, capacities 500 to 750 cc., permits the passage of 6 to 8 amperes, or more, of current through the coil and solution by water-cooling the space between beaker and cylinder.

The anode is a straight doubled wire, and the cathode is a large, closed cylinder of foil, 7.5 cm. in diameter, 11 cm. high, perforated with holes 3 mm. in diameter and spaced 1 cm. apart.

In the iron determination, 25 grams of drillings are dissolved in 25 cc. nitric acid, 40 cc. sulphuric acid and 100 cc. of water; 50 grams would require 55 cc. of nitric acid, 80 cc. of sulphuric acid and 250 cc. of water.   20 grams of copper for sulphur determination would be dissolved in 120 cc. of pure nitric acid and free acid removed before diluting with water.   For arsenic test, 25 or 50 grams of metal are dissolved in nitric acid, either 40 cc. or 80 cc. of sulphuric acid added, and the nitric acid evaporated until the residue smells sweet, after which 25 or 50 cc. of nitric acid are added, the residue dissolved and electrolyzed before it has a chance to crystallize.

The use of the large rotary device is a success for the rapid separation of copper from most of the elements mentioned, but does not give as good re-

sults for arsenic as the electrolysis of 5 or 10 grams by the slow method. It requires that a precipitation of the arsenic be made in (2 : 1) HCl to remove not only antimony, but also a trace of platinum which is dissolved continuously from the anode by the nitrous acid and heavy current.

Notes on the Accurate Titration of Arsenious Acid by Iodine. — We have made many experiments to ascertain the proper conditions for the accurate titration of arsenious acid in either very small or large amount and to eliminate slight errors which some chemical authorities have declared to be inherent in the titration.

In the first place we have found that sulphuric acid is a better medium than hydrochloric acid for final solution and neutralization.

The blank tests for arsenic in the former acid or for the nitric acid used in the process are very small, but hydrochloric acid contains a variable trace of arsenic or an element which distills and affects iodine.

The following are tests on two lots of C. P. HCl, from two makers:

No.	Cc. acid taken.	Cc. of iodine.	Blank for end-point.	Cc. of iodine.	Arsenic found, grams.
1	100	0.22	0.08	0.14	0.00015
2	100	0.32	0.08	0.24	0.00027

The HCl was neutralized with ammonia, using a piece of litmus paper as indicator, cooled, made acid with one drop excess and treated with 12 grams of sodium bicarbonate; total volume, 300 cc.

The soda should be free from iron.

We also find that the titration of traces of arsenic is rendered exact if three drops of a 10 per cent solution of potassium iodide are added. This supplies the conditions for a clear end-point with 2 cc. of a starch solution made up according to directions recently published.[1] That authority directs that the starch shall be soaked 24 hours in very dilute HCl, then washed, dried, and heated 3 hours in a hot oven at 100° C. The end-point thus obtained is a remarkably delicate blue, free from the muddy reddish tint given by the ordinary starch indicator, and the blank for the amount to produce an end-point is only 0.04 cc. of iodine, of which 1 cc. = 0.001 gram of arsenic.

Most of the printed methods direct that 2 to 4 grams of sodium bicarbonate should be added to the slightly acidified solution before titration. In the titration of large quantities, or any unknown assay, we find it is an advantage to add a very much larger excess of pure soda, free from iron, as it insures a sufficient quantity of the ions present, which recent investigators have said to be necessary for the uniform action of the iodine, and the production of the iodide of starch. The use of the precautions mentioned, with cooling of the solution before the final addition of the bicarbonate of sodium, enables an operator to titrate a milligram of arsenic, or 100 mg., as closely as one can precipitate it by magnesia and weigh it, and with more certainty for small amounts.

[1] Chem. Abs., 4, 2617, 1910.

The iodine solution is made by dissolving 3.5 grams of pure resublimed iodine and 7 grams potassium iodide in water, diluting to one liter, and allowing to stand in a brown bottle for at least 24 hours before use.

A 10 per cent solution of potassium iodide is also made and 3 or 4 drops are added to every titration, after the bicarbonate of soda.

Standardize with pure arsenious acid, of which 0.06-gram portions are dissolved cold in a little water containing 1 gram, or less, of potassium hydrate, washed into a No. 3 beaker, diluted to nearly 300 cc., made slightly acid with sulphuric acid, using litmus paper as an indicator.

Make slightly alkaline with ammonia, then faintly acid with one drop in excess of the acid, add the carbonate, and titrate rapidly until the end-point is nearly reached, employing 3 cc. of starch solution as the indicator and 3 drops of the 10 per cent solution of KI.

The beaker is allowed to stand on a white surface and a fainter end-point is noted and taken with less than 5 mg. arsenic than when the quantity is large.

A thermometer is attached to the burette when standardizing and during the regular work, and a correction is made to the burette readings for changes in the volume of the solution from that prevailing at the time of the standardization.

A table shows the agreement in the titration of varying amounts of arsenic with an ordinary untreated starch indicator, which causes a higher

blank test as shown. Results with the new starch are better, so much so that we now prefer to titrate arsenic in accurate analysis, rather than to weigh it.

As taken.	Iodine, total cc.	Blank test.	Net cc. of iodine.	Arsenic found, gram.
0.0010	0.99	0.09	0.90	0.0010
0.0020	2.02	0.09	1.93	0.00214
0.00206	1.86	0.09	1.77	0.00196
0.0024	2.27	0.09	2.16	0.0024
0.0020	1.91	0.09	1.82	0.00202
0.00998	9.12	0.09	9.03	0.01002

TABLE OF FACTORS FOR USE IN ALLOY ANALYSIS

Precipitate.	Sought.	Factor.	Logarithm.
Al_2O_3................................	Al	0.53034	−1.72455
$AlPO_4$.................................	Al	0.22195	−1.34625
Sb_2O_4................................	Sb	0.78975	−1.89749
Sb_2S_3.................................	Sb	0.71418	−1.85381
Sb......................................	Sb_2O_4	1.26623	0.10251
As_2S_3.................................	As	0.60923	−1.78478
As_2S_5.................................	As	0.48332	−1.68424
$Mg_2As_2O_7$.......................	As	0.48287	−1.68383
Bi_2O_3.................................	Bi	0.89654	−1.95257
$BiOCl$..................................	Bi	0.80208	−1.90422
Bi_2S_3.................................	Bi	0.81216	−1.90964
$CdSO_4$................................	Cd	0.53916	−1.73172
$Cd_2P_2O_7$..........................	Cd	0.55946	−1.74779
$CoSO_4$................................	Co	0.38035	−1.58019
$3K_2SO_4.2CoSO_4$.................	Co	0.14160	−1.15107
Cu_2S..................................	Cu	0.79858	−1.90232
CuO...................................	Cu	0.79892	−1.90250
$Cu_2(CNS)_2$..........................	Cu	0.52260	−1.71815
Fe_2O_3................................	Fe	0.69943	−1.84475
Fe......................................	Fe_2O_3	1.42971	0.15525
$PbSO_4$................................	Pb	0.68311	−1.83449
PbO_2.................................	Pb	0.86616	−1.93760
$PbCl_2$.................................	Pb	0.74492	−1.87211
$Mg_2P_2O_7$...........................	Mg	0.21847	−1.33938
MnO_2................................	Mn	0.63189	−1.80064
Mn_3O_4...............................	Mn	0.72027	−1.85749
$Mn_2P_2O_7$..........................	Mn	0.38702	−1.58773
NiO...................................	Ni	0.78576	−1.89529
$Ni(C_8H_{14}N_4O_4)$.................	Ni	0.20325	−1.30804
$NiSO_4$................................	Ni	0.37919	−1.57886
$Mg_2P_2O_7$...........................	P	0.27847	−1.44478
$BaSO_4$................................	S	0.13738	−1.13792
SnO_2.................................	Sn	0.78808	−1.89657
Sn......................................	SnO_2	1.26891	0.10343
ZnS...................................	Zn	0.67199	−1.82736
$Zn_2P_2O_7$...........................	Zn	0.42914	−1.63260

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